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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

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Editors are permitted to publish abstracts, providing that acknowledgment is made to The Institution of Petroleum Technologists.

Issue of Journal. The Journal is issued in six parts per volume, commencing in February of each year, with occasional extra numbers when necessary. The Title Page, Table of Contents and Index to each volume are published in the first issue of the succeeding volume.

Members whose subscription is not in arrear receive the Journal free of cost, and additional copies are charged at the rate of 7s. 6d. per part, unless otherwise stated. A member whose subscription is not paid by June 30th of the year for which it is due is considered to be in arrear.

Changes of Address. Members are requested to notify any change of address to the Secretary.

Papers and Articles. Members are invited to submit papers to be read at the General Meetings of the Institution, and are specially asked to forward articles for consideration for publication in the Journal. Diagrams, illustrations, etc., should be suitable for direct photographic reproduction.

Authors of papers published in the Journal are entitled to receive 25 free reprints of their contribution. Further copies may be obtained on payment and orders for these should be sent to the Secretary when the manuscript is forwarded to the Editor. The free reprints do not include any discussion which may be published with the paper, but authors may have such discussion included in their reprints on payment of the additional cost.

Galley proofs of the paper to be read at a General Meeting are available at the time of the meeting, but members desirous of receiving such galley proofs in advance should apply to the Secretary.

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Abstracts. Abstracts of the more important articles and patent specifications are published with each issue of the Journal, this supplement being paged independently of the transactions. Members desiring to have the Abstracts printed on one side of the paper only can be supplied with uncorrected galley proofs at a charge of 10s. per annum per copy, payable in advance.

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A medal and a prize of five guineas is awarded annually by the Council to that Student Member of the Institution who shall, in their opinion, have presented the best paper during the session.

Research Fund. The sum of £400 is allocated in each calendar year to the advancement of Research in Petroleum Technology and its basic sciences, and the Council are prepared to receive applications for assistance from this fund.

Applications from persons proposing to engage in research in any university or other teaching institution must be supported by the professor under whom the applicant will be working.

Applications from Associate Members, Students or Associates of the Institution of Petroleum Technologists and non-members, not proposing to engage in research in any university or other teaching institution, must be supported by a Member of the Institution or other responsible person.

Applications from full Members of the Institution do not require a supporter.

Applications for grants from this fund will be considered in June and December of each year and must be received by the Secretary not later than June 1st or December 1st respectively. Application forms may be obtained from the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2.

Advertisements. Advertisements are inserted in the Journal, and information as to terms, etc., can be obtained from Mr. Thomas Tofts, 304, Bank Chambers, 329, High Holborn, W.C. 1. (Telephone No. Hol. 4776.)

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Library. The Institution's Library may be consulted between the hours of 11 a.m. and 4 p.m. daily. (Saturdays, 11 a.m. to 1 p.m.)

ADDITIONS TO THE LIBRARY SINCE THE LAST JOURNAL.

The Geology of Venezuela and Trinidad. By R. A. Liddle. 1927.

Fuels and their Combustion. By R. T. Haslam and R. P. Russell. 1926.

Solid Bitumens, their Physical and Chemical Properties and Chemical Analysis. By S. F. Peckham.

Coal Carbonisation, High and Low Temperature. By J. Roberts. 1927.

Practical Oil Geology. By Dorsey Hager. 1926.

From the Oil Well Supply Company :—

"Oilwell" Oil Field Equipment. No. 45. Catalogue.

From M. Pierre Viennot :—

"Le gisement Pétrolifère de Gabian." 1928.

ARGENTINE.

Anales de la Oficina Quimica de la Provincia. Tomo 1. No. 2. 1928.

DUTCH EAST INDIES.

Jaarboek van het Mijnwezen in Nederlandsch-Indie. 1926.

U. S. A.

From the U.S. Bureau of Mines :—

Circular No. 6049. October, 1927. Railroad Fuel Oil Consumption in 1926. By A. H. Redfield.

Circular No. 6050. October, 1927. Sources and Distribution of Major Petroleum Products, Atlantic Coast States. 1926. By E. B. Swanson.

Circular No. 6061. February, 1928. Sources and Distribution of Major Petroleum Products, Central United States. 1926. By E. B. Swanson and A. H. Redfield.

Circular No. 6064. April, 1927. Accident-prevention Work of the Mid-West Refining Company. By E. H. Denny.

Circular No. 6071. May, 1927. Exports of Mineral Oils from Gulf Coast Ports in 1927. By A. H. Redfield.

Serial No. 2857. February, 1928. A Comparison of Ground Temperatures at Different Depths and Temperature Fluctuations of the Atmosphere. By E. L. Rawlins and T. W. Johnson.

Serial No. 2862. March, 1928. A Rapid Corrosion Test for Gasoline. By H. P. Rue.

Bulletin 291: Tabulated Analyses of Representative Crude Petroleums of the United States. By N. A. C. Smith and E. C. Lane. 1928.

Technical Paper 414. Methods of Dealing with Paraffin Troubles encountered in Producing Crude Oil. By C. E. Reistle, Jr. 1928.

Petroleum in 1926. By G. R. Hopkins and A. B. Coons.

From the U.S. Geological Survey :—

Bulletin 788-F.: Topographic Instructions of the U.S. Geological Survey. F. Map Compilation from Aerial Photographs. By T. P. Pendleton. 1928.

Bulletin 769-B: Geology and Oil and Gas Prospects of North-Eastern Colorada. By K. F. Mather, J. Gilluly and R. G. Lusk. 1928.

Bulletin 796-C: Geology and Coal Resources of the Salina Canyon District, Sevier County, Utah. By E. M. Spieker and A. A. Baker.

Bulletin 796-D: Geology and Oil and Gas Possibilities of the Bell Springs District, Carbon County, Wyoming. By C. E. Dobbin, H. W. Hoots and C. H. Dane.

Bulletin 797-A: Mineral Industry of Alaska in 1926 and Administrative Report. By Philip S. Smith.

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. T. L. BONSTOW is now in England.

Mr. R. BROADHURST is now in Ecuador.

Mr. W. E. D. COLE has returned from Persia.

Mr. E. H. CRUSH is home from India.

Mr. A. G. ENGELBACH is home from Persia.

Mr. W. N. FOSTER is in Peru.

Mr. A. LLOYD has left for Burmah.

Mr. W. MOORE is now in England.

Mr. J. H. PARK has left Irak for Persia.

Mr. M. A. RUST is now in the Farsan Islands.

Mr. A. J. RUTHVEN-MURRAY is now in England.

Mr. R. H. SPERLING is in Canada.

Mr. H. LE M. STEVENS-GUILLE has returned from Burmah.

Baron G. VAN WASSENAER is now in Holland.

Mr. L. F. WHITFIELD has left Canada and is now in Colombia.

Mr. C. A. H. WILLIAMS is leaving for Trinidad.

Mr. L. J. WILMOTH is returning to Burmah.

Mr. S. G. WRAIGHT is now in Aruba.

The Secretary will be glad to receive information as to the whereabouts of the following members:—J. M. BAILEY, G. M. GREAVES, D. H. GWINNER, L. B. HOLLOWAY, K. C. JOHNSON, I. C. LOW, E. C. MASTERSON, J. K. WALTON and S. S. WEBB-BOWEN.

The suggestion has been made that complete bound sets of the Journal should be available for sale to members of the Institution. Any member wishing to avail himself of this opportunity should communicate with the Secretary.

The engraving of the members of the Institution, made by Messrs. H. J. Whitlock and Co., is now ready, the cost being £10 10s., £7 7s. and £5 5s., together with the key. For the convenience of members, a photograph of the engraving has been made, size 14 in. by 10½ in., at a cost of £1 1s., inclusive of the key.

Application for copies of the engraving or the photograph should be made to Messrs. H. J. Whitlock and Co., Cory's Building, Fenchurch Street, London, E.C. 3.

We have received from Messrs. British Geophysical Survey, Ltd., 3-4, Clement's Inn, London, W.C. 2, a copy of their brochure on Geophysical Surveying.

The subject of Geophysical Surveying is dealt with in a practical way, and is illustrated with pictures of the various types of instrument. Copies of this interesting brochure may be obtained on application to the above-mentioned firm.

OBITUARY.

F. Mollwo Perkin, C.B.E., Ph.D., F.I.C., F.C.S.

We regret to have to announce the death of Dr. F. Mollwo Perkin on May 24th, 1928. Dr. Perkin, who was 58 years of age at the time of his death, was an Original Member of the Institution and was elected a Member of Council at the first Council Meeting on May 14th, 1914. He resigned from the Council on February 3rd, 1925.

Dr. Perkin was the author of several papers published in the Journal of the Institution, and often contributed to discussions on subjects connected with low-temperature carbonisation.

STANDARD METHODS OF TESTING PETROLEUM AND ITS PRODUCTS.

In view of the proposed publication during the coming year of a second edition of "Standard Methods of Testing Petroleum and Its Products," it has been decided that the remaining copies of the first edition shall be made available at 3s. per copy on and after January 1, 1928.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

In connection with the Physical and Chemical Survey of the National Coal Resources, a Committee has been formed to deal with the South Wales Coalfield. The Committee is composed of

representatives of the Monmouthshire and South Wales Coal Owners' Association, the South Wales Institute of Engineers, the Geological Survey of Great Britain and the Department of Scientific and Industrial Research, and will investigate the characteristics of the various coal seams in the South Wales area with a view to their utilization to the best advantage.

WORLD POWER CONFERENCE.

Fuel Conference, 1928.

The 1928 Fuel Conference of the World Power Conference will be held at the Imperial Institute, London, from September 24th to October 6th. The fees for Membership of the Conference are 30s., with a reduced fee of 20s. for Members of participating bodies, and application forms can be obtained from the Secretaries, Fuel Conference, 1928, World Power Conference, 36, Kingsway, London, W.C. 2.

During the Conference, papers dealing with topics of vital importance to the fuel industry will be read and discussed, and the following list gives the papers dealing with petroleum and allied substances :—

"The Economics of the Oil Industry, including the Influence of By-Products." E. H. Davenport.

"Modern Developments in Oil Distillation." Dr. A. E. Dunstan and J. Kewley.

"Modern Developments in Oil Refining." Dr. A. E. Dunstan and J. Kewley.

"Modern Developments in Oil Cracking." Dr. A. E. Dunstan and J. Kewley.

"The Technical Aspects of the Storage, Handling and Transmission of Liquid Fuels by the User." I. Lubbock.

"The Production of Gaseous Fuels from Liquid Fuels." J. Kewley.

"Fuel Oil for Steam Raising." Comdr. A. P. L. Mark-Wardlaw, R.N.

"Industrial Heating by Solid, Liquid and Gaseous Fuels." Sir Robert Hadfield, Bt., F.R.S., and R. J. Sarjant.

"A Comparative Study of Solid Fuel, Gas, Electricity and Oil for Domestic Purposes." Dr. Margaret Fishenden.

"The Properties of Motor Spirit in Relation to Engine Design." H. R. Ricardo.

"Fuel Oil for Heavy Oil Engines." Harold Moore.

"The Transmission of Power over Various Distances by the Alternative Methods of the Transport of Coal, the Transport of Oil, the Transmission of Gas and the Transmission of Electrical Power." Dr. E. W. Smith.

"Low Temperature Carbonisation." Dr. C. H. Lander, C.B.E., and Dr. F. S. Sinnatt.

"The Training of Fuel Technicians." Professor J. W. Cobb.

"Technical Data on Fuel." H. M. Spiers.

Copies of the papers to be read before the Conference will be available to Members of the Conference only and can be obtained in advance.

NEW INTERNATIONAL ASSOCIATION FOR TESTING MATERIALS.

At a Congress in Amsterdam in 1927, the New International Association for Testing Materials was formed and, in order to secure adequate British representation in the Association, a British Committee has been formed, consisting of representatives of a number of British Institutions and Societies.

Members of the constituent bodies are invited to join the N.I.A.T.M., the subscription being the nominal sum of 10s. per annum. Membership forms and full particulars are obtainable from the Hon. Secretary, G. C. Lloyd, Esq., 28, Victoria Street, London, S.W. 1, or from the offices of the Institution.

STANDARD METHODS OF TESTING PETROLEUM AND ITS PRODUCTS.

Report of the Standardization Committee, giving details of Methods of Test for Petroleum and Its Products.

Price: **3s.** net.

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DECENNIAL INDEX, 1914 to 1924.

The complete index to the first ten volumes of the Journal of the Institution contains some 10,000 references to subjects and localities.

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THE PETROLEUM INDUSTRY.

A brief survey of the Technology of Petroleum based upon a Course of Lectures given by Members of the Institution of Petroleum Technologists at the Petroleum Exhibition, Crystal Palace, 1920.

This work will be found of value to students and those desirous of obtaining an elementary knowledge of the Technology of Petroleum.

A few remaining copies for disposal at **2s. 6d.**

REPORT OF THE EMPIRE MOTOR FUELS COMMITTEE.

The complete Report of the Empire Motor Fuels Committee, containing valuable data relating to Fuels for Internal Combustion Engines.

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All the above to be obtained from the office of the Institution,

ALDINE HOUSE, BEDFORD STREET, STRAND, LONDON, W.C. 2

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The One Hundred and Tenth General Meeting of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, W.C. 2, on Tuesday, April 3rd, 1928, Mr. Alfred C. Adams, President, occupying the Chair.

The President, at the opening of the meeting, said there was no need for him to introduce the reader of the Paper, Dr. Wade, who was well-known not only for the other Papers he had read before the Institution but for his investigations of geological features in connexion with petroleum finding in different parts of the world. The Paper that was about to be read dealt with the question of the finding of petroleum nearer at home, namely, "The Oil Well and Later Developments at Hardstoft, Derbyshire." It was a subject which greatly interested many people at home, and he had no doubt it would evoke much comment.

The following Paper was then read :—

The Oil Well and Later Developments at Hardstoft, Derbyshire.

By Arthur Wade, D.Sc., A.R.C.Sc., etc. (Member)

I. Introduction.

The history of the effort made by the Government during the late years of the war period to discover whether oilfields existed in this country is well-known to members of this Institution. Papers on the subject have appeared in both British and American publications but not, unfortunately, in our own Journal. After a long period of geological investigation, eleven wells were sunk to depths ranging between 1,810 feet and upwards of 4,000 feet, only two of which met with anything like success, the well at Hardstoft in Derbyshire and the Darcy well near Edinburgh. Of these the former, the first to be commenced, is the only one which has produced, and is still producing oil in any considerable quantity, the only one which has ever looked like a commercial proposition. These facts are well known, but this oil well in England seems to have aroused little interest, even where such interest might naturally have been expected. On the other hand, nothing has been published concerning the two later wells which have been drilled at Hardstoft since 1924. In course of conversation with Captain J. D. Penrose, agent for the Duke of Devonshire, it was suggested that I should look over the Hardstoft area and

through the detailed records and history of operations, which Captain Penrose has very ably preserved, with the object of submitting the more important facts to this Institution. I am, therefore, indebted to him for most of the material for this paper.

II. Hardstoft No. 1.

Oil in quantity was struck in Hardstoft No. 1 well on the night of May 27th, 1919, at a depth of 3,070 feet, in a sandy limestone near the top of the main Carboniferous Limestone sequence. Giffard[4] states that the producing horizon is two feet in thickness, but there is nothing in the drilling records to confirm this. Ickes[5] states that the production was obtained from beneath a hard shell at the top of the Mountain Limestone in a sandy limestone member probably not more than five feet thick. On the other hand the drillers log "sand" down to 3,085 feet, which indicates a producing horizon possibly 15 feet in thickness. This uncertainty is characteristic of the records with regard to this well. The story of what preceded this happening has been dealt with in some of the papers referred to. It is important to note that a fuller and more detailed account exists in Captain Penrose's unpublished records. Between that date and December 31st, 1927, the well has produced approximately 2,500 tons of oil, or about 20,000 U.S. barrels—an average of over six barrels a day for 8½ years, which compares favourably with the official statements of the daily average yield of producing wells in the U.S.A.

The oil is of very good quality and resembles Pennsylvanian crude. It is of light gravity and has a paraffin base. The table shows three analyses for comparison, there being slight differences between the results obtained.

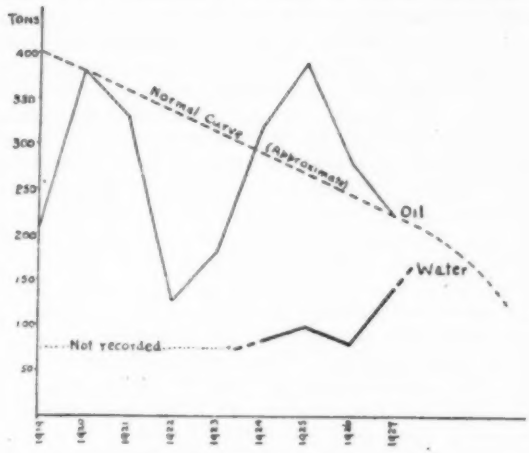
1.* Sp. gr. 40 Bé.	%	Sp.gr.	Bé.	2.† Sp. gr. 0·823	%	3.‡ Sp. gr. 0·828.	%
Gasoline ..	10	0·720	65	Motor spirit	7·5	Fraction boiling up to 150° C.	4·5
Kerosine ..	30	0·7835	48	Kerosine...	39·0	do. 300° C.	45·5
Light lubricating oil and wax	30	0·838	37	Gas oil ..	20·0	do. between 300° C. and 400° C.	—
Heavy lubricating oil	30	0·893	27	Lubricating oils ..	30·5	Residue over 450° C.	—
Sulphur ..	0·42			Sulphur ..	0·26		
Wax ..	3·25			Paraffin wax	3·0	Wax in original oil ..	3·2
Paraffin base containing naphthenes.				Setting pt. 0° F. Viscosity at 100° F. Red. 48 secs.		Ash	0·036

The oil is dark brown in colour with green fluorescence. Giffard[4] states (p. 15) that "An important feature of this oil is the presence

*[5]. †[4] After Hackford, p. 15. ‡[7] After Dr. A. R. Bowen, p. 2.

in the lubricating fractions of a high percentage of oils suitable for steam-cylinder lubrication which have hitherto been obtained almost exclusively from Pennsylvanian crude."

The curve showing the yearly production of petroleum from this well, since it commenced to flow at the end of May, 1919, up to December 31st, 1927, is of interest. It is a very abnormal production curve for an oil well, and it tells quite plainly its own story of hesitancy in handling, irregular pumping and change of ownership. The well was drilled by the Government under D.O.R.A. on property belonging to the Duke of Devonshire. It seems quite clear that nobody had really expected a pro-



PRODUCTION CURVE, HARDSTOFT NO. 1.

ductive oil well which was rather a source of embarrassment than otherwise. After the partial repeal of D.O.R.A. the Duke of Devonshire took the well over from the Government. A licence to conduct operations upon his own property was not, however, obtained until June, 1923. The condition of the well at this time can be deduced from the curve. From the end of May, 1919, when the well first came in, to December 31st, 1919, the production of oil as given by Ickes was 1,666 U.S. barrels. A later report states that 2,568 barrels of oil were produced during this period. In 1922, production had fallen to 974 barrels, or about 125 tons. Ickes and others did not regard this as a normal decline, and attributed the fall to the waxing up of the sand around the well. The rest of the curve shows

that their views were well founded. The rapid decline in early production suggests a study of the way in which the well was brought in. The logs seem to have been very loosely kept at this time. There is no record of pipe being lowered beyond 2,997 feet, though there is a later note to the effect that the length of the 8-inch casing is 3,002 feet. At the bottom of this 83 feet of 6 ⅝-inch liner is logged, but there is nothing to show whether it is perforated or not. It was found later, though again the fact was not logged, that the top of this liner stood 3 feet 6 ins. above the base of the 8-inch casing, which brings the shoe of the liner to a point 7 feet below the horizon at which oil was found. It was originally intended to shoot the well, as is usual with wells in limestone in the U.S.A., but the 8-inch casing was found to be frozen in the hole and the carriage of nitroglycerine over public roads in England is prohibited by law, so this was not done. In the circumstances it is remarkable that the well produced and continued to produce as much oil as it has done. The conditions existing at the bottom of the hole have never favoured a full and free flow of oil into the well, and have tended to promote waxing and silting. On the advice of Mr. A Frank Dabell and Dr. Henderson the well was cleaned out as well as was possible in 1923, the result being a rapid rise in production during the years 1924 and 1925—the highest yearly yield being recorded in the latter year; that is to say in the sixth year of its life which is again an abnormal feature. When the well was being cleaned out it was found that not only had the well filled in to a depth of 25 feet, but it was half full of water, though it was reported to be quite dry when oil was struck, and the oil which first came into the well was quite free from water. It is thought that the water may be from a water sand, found at 1,515 feet and not cemented off, and is now finding its way through a defect in the 10-inch casing near this level. Another possibility is that water has broken in around the shoe of the casing.

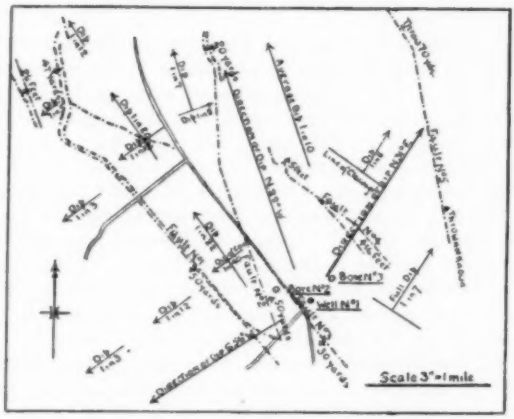
Since 1925 there has again been a marked decline in production though not so rapid as in 1921. This again may be due in part to waxing and silting though the fact that this decline in oil production has been accompanied by a rapid increase in the amount of water produced, as shown in the lower curve, may mean that bottom water is now gaining on the oil. Against this is the fact that the water found at this horizon in the No. 2 bore proved on analysis to be quite different in character.

The broken curve which I have run across the actual production curve of the well is, I think, an approximation to what should have been the normal production curve. Judging from normal curves from producing wells in other oilfield areas it would indicate that

at least three further years of productive life may be expected for this well.

III. Geology of the Hardstoft Area.

Before proceeding to discuss the second and third wells at Hardstoft I should, perhaps, briefly recapitulate the geology of the Hardstoft area. Radiating from the central Pennine axis in the Peak district a number of subsidiary, anticlinal folds run out E. and W. into country capped by the varied strata of the Coal Measure Series. Subsurface contouring on the well-known coal seams shows that these folds are broken into well-marked dome structures. Hardstoft No. 1 is situated on the crest of one of these domes, the long axis of which runs from N.W. to S.E. for over one mile and continues still further to the S.E. on a plunging axis. The more detailed underground structure of these domes is unusually well known owing to the working of coal seams in their vicinity. At Hardstoft the folding is accompanied by considerable faulting. Both folding and faulting are well shown on diagram No. 2. It will be seen that some half mile



FAULT AND DIP DIAGRAM—HARDSTOFT.

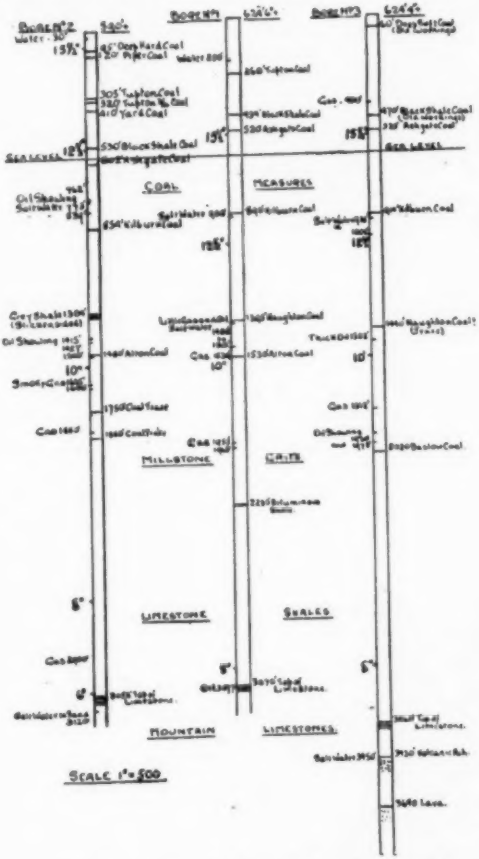
to the E. of Hardstoft No. 1 there is a considerable fault (No. 5 diagram No. 2) with an easterly throw which has been found to be 70 yds. to the N.E. of the well. Minor faults (e.g. No. 4) still throwing down to the E. come between this fault and the well. To the W. of the well are three other considerable faults. No. 3, about 70 yds. to the W. of the well,

has a throw of about 30 yds. to the W. This fault was not discovered until the second well was drilled and a good show of oil was met with near the horizon of the Kilburn Seam just about the intersection of this fault with fault No. 2. No. 2 fault lies about 250 yds. to the W. of Hardstoft No. 1, and again throws down to the E. to the extent of 50 yds. The normal hade for such faults in this district is 75°, and in choosing the site for the No. 1 well Mr. Ickes states that it was intended to strike the intersection between this fault and the top of the Carboniferous Limestone. Some controversy has arisen as to whether this was done or not. About 150 yds still further to the W. is another considerable fault, No. 1 throwing down the measures 50 yds. to the W. This fault, as proved in the coal workings, is 22 yds. thick and is found to be vertical, the low hade shown for this fault on some of the earlier sections through Hardstoft being incorrect. From a centre at which the No. 1 well is placed the beds dip pretty evenly in almost every direction, generally at from 5° to 10° though higher dips may be seen locally, especially on the S.W. flank of the fold.

IV. The Second Boring at Hardstoft.

Dr. J. A. L. Henderson was given the responsible task of selecting the site for the second boring at Hardstoft. As previously stated the site for No. 1 was carefully selected with the idea of striking the intersection between fault No. 2 and the surface of the Carboniferous Limestone. The geologists employed consider that this was not done. Ickes states that in his opinion this fault was passed through at a depth of between 1,350 and 1,550 ft., that the hade of the No. 2 fault was less than was thought, being about 60°, and that the line of intersection between the two surfaces would be about 1,000 ft. to the E. of well No. 1. On these assumptions Dr. Henderson had good grounds for believing that the productive area should exist between the intersection of fault No. 2 with the top of the limestones and the vertical No. 1 fault. The site for the second boring was, therefore, chosen about 600 ft. to the W. of well No. 1. It was expected that exactly the same sequence of strata would be met with in No. 2 as in No. 1. The drilling was started on May 16, 1924 with an 18-in. hole, with the intention of inserting a small string of 15½-in. casing to act as conductor pipe. A number of surprises awaited. The first was an unexpected water sand at 30 ft. which led to more 15½-in. casing being used than was intended. This was landed at 71 ft. and the top water shut off. The next surprise was the striking of a coal seam at 100 ft. which was not expected before a depth of 230 ft. was reached. The upper strata also proved to be harder and more

difficult to drill than in No. 1. Further coal seams were met with and recognised, and it now became evident that an unsuspected fault (No. 3) ran between Bores No. 1 and No. 2 having a down



VERTICAL SECTION OF BORES AT HARDSTOFT.

throw to the W. of 30 yds. The ground was becoming more and more broken, so much so that the Black Shale Coal Seam, the most important in the district, was only recognised with difficulty in the cuttings. At 600 ft. there was a strong and troublesome

flow of mud and at 760 ft., about the horizon of the Kilburn Seam, a good show of oil, sufficient to yield a 10-gallon sample after the well had stood for 24 hours. Analysis of this gave the following results:

Specific gravity at 60° F., 0·862.

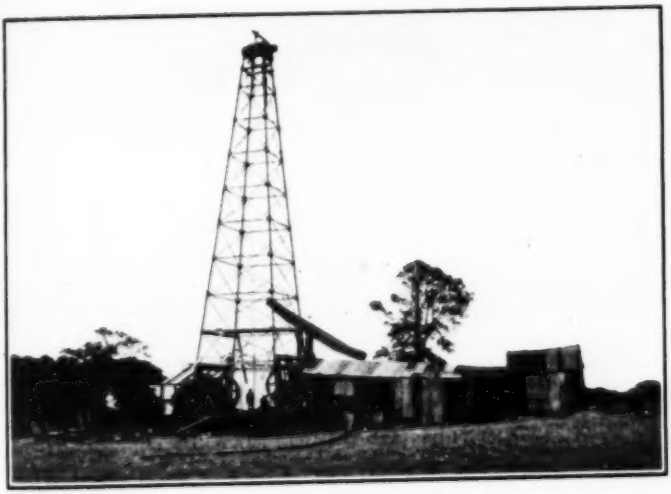
Vol. to 150° C.	(Petrol)	..	2·5°		
,, 150—300° C.	(Kerosine)	..	22.5°	Sp. gr. at 60° F.	0·794
Residue	(Fuel oil)	..	74·0°	,, ,,	0·885
Sulphur	.. ..	..	0·16°		

Salt water in small amount was met with a few feet below this. It is thought that the bore passed through the intersection between faults No. 2 and No. 3 about this level. At 840 ft. a strong flow of water was encountered, and this caused the broken formation above to cave badly and the hole completely collapsed. After the expenditure of much time and trouble this was partly got over and the caving ground was held up by 12¾-in. casing at 840 ft. The water, however, was not shut off and, unfortunately, more faulty ground was met with almost immediately at 860 ft. This compelled the drillers to set the 10-in. string at 903 ft. and the water was shut off for the time being. Further water was expected at 1,350 ft., but it was not found until the well had been deepened to 1,515 ft. This water was at exactly the same level as an important water horizon in well No. 1, but whereas in the latter the flow was very considerable in amount, 10 bailers per hour, only a negligible flow of brackish water was encountered in No. 2. After a lot of trouble with caving and fishing for lost tools, the hole was finally under reamed and the 10-in. casing carried to 1,546 ft. and there successfully set in cement. From this point drilling was more straightforward, and the 8-in. casing was finally set at 2,600 ft. A flow of gas, about 20,000 cubit ft. per 24 hours, at a pressure of 370 lb. per square in. was struck at 1,620 ft., and it was found possible to utilise this as fuel for boilers by passing it between the 8-in. and 10-in. casing, a packing head with a flow pipe being arranged at the top of the casing for this purpose.

From 2,600 ft. an open hole was drilled for 6⅝-in. casing until caving shales became dangerous. However, by inserting the 6⅝-in. casing, drilling ahead with a 6-in bit and under reaming, good progress was made. The two bottom lengths of the casing were perforated.

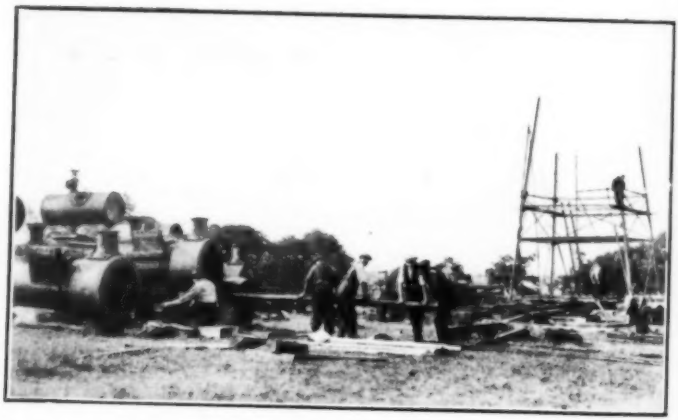
It was expected that the oil sand would be met with at around 3,050 ft. but nothing but a trace of oil was found at the producing horizon of the No. 1 well and at a depth of 3,056 ft. The hole was carried to 3,125 ft. where a strong flow of salt water was struck, continued to 3,130 ft. where, owing to a troublesome influx of sand, drilling ceased. This water kept a constant head of

HARDSTOFT NO. 1 FLOWING.



HARDSTOFT, No. 3 BORE.

CASING FLATTENED BY WATER PRESSURE, HARDSTOFT NO. 3.



SETTING UP RIG AND DERRICK, HARDSTOFT NO. 3.

2,800 ft. in the hole and could not be bailed down. The well was, therefore, plugged with cement and abandoned on March 24th, 1925, though the gas from this well is still being utilised. The actual time spent in drilling No. 2 was 313 days, but fishing jobs and under-reaming took up nearly half of that time.

Analysis showed that the water found at the bottom of the second well was quite different from the water coming in with the oil in No. 1, although this well was also carried to a depth of 3,130 ft.

	Bottom Water. Hardstoft No. 1. Parts per 100,000.		Bottom Water, Hardstoft No. 2. Parts per 100,000.
Suspended matter (organic)	135		
Suspended matter (inorganic, mainly ferric oxide)	114		
Total dissolved solids	1608		
SiO_2	none detected	..	1·20
Iron (as Fe_2O_3)	17·6	..	0·80
Calcium (as CaO)	177·2	..	320·50
Magnesium (MgO)	32·4	..	106·14
Zinc (ZnO)	—	..	3·75
Sulphates (SO_4)	139·6	..	68·68
Carbonates (CO_3)	29·6	..	5·10
Alkali chlorides	1034·0	..	2092·30
Undetermined and difference	157·5	..	—
	1608·00		2598·47

V. Hardstoft No. 3.

The failure to find oil in Hardstoft No. 2 was, naturally, a great disappointment. In spite of this it was decided to try again. A period of negotiation followed upon the conclusion of which the Anglo-American Oil Company undertook the responsibility of putting down a third borehole. Mr. W. P. Haynes, geologist for the company, selected a site 600 ft. somewhat N. of E. of the No. 1 well, and drilling commenced on August 5th, 1925. As before, work commenced with an 18-in. hole in very hard rock known locally as the Potter's Rock, and delays were caused by breakages, the tools proving too light for the ground. The tool joints used were $3\frac{1}{4}$ in. $\times 4\frac{1}{4}$ in. $\times 7$ in. instead of the 4 in. $\times 5$ in. $\times 7$ in. joints more commonly used for heavy work.

At 60 ft. old workings in the Deep Soft Seam were met with, which was of interest, since it was not known that this seam had been worked in this locality. A little water came in from the workings, but otherwise no trouble was experienced. A small show of gas was accidentally discovered at 400 ft., an explosion occurring when a driller dropped a light into the hole. This gas, however, may have found its way into the hole from the old

workings. At 470 ft. old workings in the Black Shale Seam were passed through, but again no difficulty, beyond loss of drilling water, and a little caving was caused owing to the fact that the fillings were solid in the workings. When drilling near this point the head driller and colliery manager managed to get within a hundred feet of the borehole by means of a disused roadway in the Tibshelf Pits with the object of observing what effect the drilling operations were having on the workings. So far as could be seen, the pounding of the bit was having no effect whatever on the old road.

The 15½-in. casing was cemented at 530 ft. just below the Ashgate Coal, and work was continued with a dry hole. It was intended to set the 12¼-in. string at about 950 ft. to shut off a water expected at between 910 and 920 ft. This calculation was accurate, the water being found in fine sandstones below the Kilburn Seam at 917 ft. Water, however, continued to be found in increasing quantities down to 947 ft., in fact the sandstone formation was water-bearing to 1,003 ft., which was not expected. The 12¼-in. string, therefore, was carried further and set in hard rock at this point. Good progress was made in shales and sandstones after this, the Alton, or Naughton, Seam being recognised with difficulty at about 1,440 ft. A show of thick oil was noted between 1,500 and 1,509 ft.

It was estimated that the water met with in No. 1 at 1,515 ft. would be found at about 1,540 ft., but as there was no evidence of it down to 2,000 ft. it was decided to try to carry the 12-in. hole to the oil horizon expected at about 3,200 ft. Shows of gas were encountered in thick sandstones, the Ganister Beds, at 1,812 and 1,823 ft. and thick oil at 1,900 and 1,978 ft. in hard shales. This oil resembled that found in No. 2 at 740 ft. At 2,020 ft. the Baslow Seam, the lowest in the district, was picked up and was followed by hard micaceous sandstones. A fault is suspected to cross the hole at about 2,180 ft. There was some caving at this point, and fragments of slickensided shale were picked up by the bailer. This is about the point where fault No. 2 should cross the boring if Mr. Ickes' conclusions are correct. It was now found that the hole was making a little water, probably from the horizon at which the 12¼-in. casing was set. In the No. 2 well caving shales became dangerous at 2,800 ft. but in No. 3 the shales began to cave very badly at 2740 ft. and progress became so difficult that the 8-in. casing was run in and cemented in soft shale at 2,809 ft. Caving, however, continued to cause much trouble. The 6⅝-in. casing was run in and taken out again, casing shoes were lost and finally it was decided to cut the 8-in. casing at 2,550 ft. Before this could be done the joint immediately

below this point collapsed, but fortunately it was found possible to withdraw it. It was completely flattened out, by excessive pressure of water, for its entire length. A 10-in. string was then run in and cemented at 1,569 ft., and preparations were made to drill past the 254 ft. of 8-in. casing left in the hole. This was first cemented in and the hole was redrilled to a point 30 ft. below the top of the lost casing. From this point it became evident that an entirely new hole was being drilled quite clear of the old 8-in. casing and, what was more, it was now dry. The 8-in. was finally landed at 2965 ft. and no further trouble was caused by caving, but there was some delay due to fishing jobs.

The first limestone was struck at 3110 ft. but it was only a few feet thick, shales following immediately again. It is considered that the top of the Mountain Limestone was reached at 3260 ft. but no oil was met with, which was another disappointment. The hole was drilling well, so it was decided to go on till the water, usually met with in the limestone, was reached. Very surprisingly, the expected water was not found, only a little coming into the hole at 3460 ft. from a volcanic ash which was first struck at 3420 ft. At 3640 ft. the drill passed into a bed of lava which continued down to 3825 ft. On June 8th, 1926, work ceased at this point and the well was abandoned. It could have been carried much deeper, for the hole was now in good shape and the lava was drilling well, but it was very plain that the boring had failed in its object.

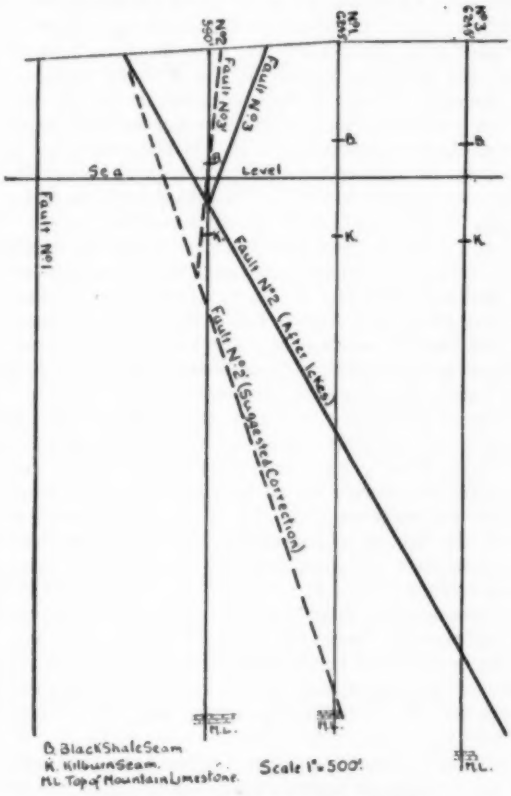
VI. Geology of the Borings.

In a general way the geological structure of the district around the boreholes is comparatively easy to determine. The numerous coal mines provide a wealth of data which increases daily as the workings extend underground. But when we come to the interpretation of the facts as presented by the logs of these three wells with distances of only 600 ft. between them, we find a problem bristling with difficulties. Oil is discovered in one well, none in the others on either side; a great quantity of water in the Mountain Limestone in the second well, none in the other two; a problem of faulting upon which, apparently, no two geologists are agreed.

Beginning with the simpler matters all three borings commence in the Coal Measures, pass through the Millstone Grits, the Yoredale or Limestone Shales and end in the Mountain Limestones, but it is only possible to fix approximate boundaries between any of these formations. Individual members of the sequence of strata can, however, be recognised in the different boreholes, especially

the better developed and better known coal seams such as the Black Shale (Silkstone) Seam and the Kilburn Seam. At the surface the beds dip from the No. 1 borehole in the direction of No. 2 at about 1 in 22. Between No. 1 and No. 3 the dip is very small, the coal seams coming in only a few feet lower in No. 3. Examining the top of the Mountain Limestone in the three bores we find a little difficulty in the fact that the limestone phase begins to come in above the base of the Limestone Shales. However, it is generally agreed that the top of the Mountain Limestone is 3070 ft. below the surface in No. 1 and 3058 in No. 2. In No. 3 the first limestone near the base of the Limestone Shales was not met with till a depth of 3110 ft. had been reached and the top of the Mountain Limestone proper is considered to be at 3260 ft. That is to say, the top of the limestone occurs in No. 1 at 2445 ft. below sea level, in No. 2 at 2468, and in No. 3 at 2635. Thus No. 1 is at the highest point in the limestone, No. 2 is 23 ft. lower, making the dip of the limestone in the direction of No. 2 about 1 in 26, which is near enough to that noted above. In No. 3 the top of the limestone is 190 ft. lower than in No. 1, and this must be accounted for in some manner and especially as the lie of the limestone between Nos. 1 and 2 is apparently quite normal. Turning to diagram No. 2 we note that a 50-yard fault (No. 2) throwing down to the E cuts the surface just West of Well No. 2. A throw of 150 ft. in this direction combined with some few feet of dip gives too close an approximation to 190 ft. to be disregarded. It seems pretty obvious that the plane of Fault No. 2 must pass between wells Nos. 1 and 3, but this conclusion is not generally accepted. Only two of the faults shown in the diagram affect these boreholes, i.e., Faults Nos. 2 and 3. Most of the faults observed in this district hade at about 75° and it has been assumed that Fault No. 3, which was not known to exist before the No. 2 well was drilled and which throws down the strata to the W. has a hade to the W. of 75°. Seams higher than those found in No. 1 borehole are present and the Black Shale (Silkstone) Seam is some 125 feet lower than in No. 1, so allowing for the dip of the strata towards No. 2 the throw of the fault is approximately 30 yards to the W. The Kilburn Seam at 854 ft. was found almost exactly at the same depth below sea level as in No. 1, which suggests two things. First, that the fault No. 3 must cross the borehole above the Kilburn Seam, and second, that the strata thrown down by the fault have been tilted by faulting and dip to the W. at a greater angle than the strata below the fault. The fault must therefore pass to the W. of the Kilburn Seam, but it cannot be far away for the seam itself is apparently crushed and only traces of it were found in the cuttings. Now this crushing is evident

in the borehole for about 400 ft., between the depths of 500 ft. and 900 ft., and this rather suggests that the fault has a much steeper hade than has been assumed. An almost vertical fault is indicated. In this connexion it is important to note that fault No. 1 in the



HARDSTOFT FAULT DIAGRAM IN SECTION.

diagram was formerly thought to hade to the W. at a moderate angle.* It has since been proved in underground workings to be vertical so that a steeper hade for fault No. 3 is not improbable. Ickes came to the conclusion that fault No. 2 has a hade to the W.

* See Section shown on p. 14.

of about 60° and some confirmatory evidence of this is thought to be provided by indications of faulting in No. 1 borehole just below the Alton Coal at a depth of just over 1530 ft., which would be about the correct position if fault No. 2 has a hade of about 60°. But fault No. 3 must pass to the W. of the Kilburn Seam and cross the borehole below it, otherwise it should have been found at a much higher level than in the No. 1 borehole for fault No. 2 has a throw to the E. of 50 yards. If the Kilburn Seam is correctly placed, therefore, in the Section of borehole No. 2, it must have been thrown down by this fault just as much as in the No. 1 borehole, and the fault must cross below it. If then we draw the line of faulting from its surface trace through a point below the Kilburn Seam, it must cut the top of the limestone between boreholes Nos. 1 and 3. There is evidence of slickensiding in the shales at a depth of 1304 ft. in Bore No. 2, and if this is the depth at which the fault crosses it should intersect the limestone very nearly at the bottom of Bore No. 1. In any case the evidence is that the intersection must be between Bores Nos. 1 and 3 and the hade of the fault must be more nearly vertical than has been supposed. Throughout this reasoning I have disregarded the fact that one of the two faults, Nos. 2 and 3, may be younger than the other and would therefore displace it where the fault planes intersect. I have found no conclusive evidence to indicate the comparative ages of these faults. They may have both been formed in the same settling movement, but in drawing scale sections to represent alternative suppositions fault No. 2 was still found to cut the surface of the Mountain Limestone between wells Nos. 1 and 3, and in my opinion the intersection is nearer to the base of No. 1 bore than to that of No. 3. Another supposition which has to be made in dealing with these fault planes is that they can be represented by straight lines. My experience is that many faults which can be observed in the vertical faces of deep quarries or on the walls of precipices can not be drawn as straight lines, the planes are seen to be distinctly curved and often become steeper with depth.

As previously stated the original intention in selecting the site for the No. 1 borehole was to endeavour to strike the intersection between the surface of the Mountain Limestone and the No. 2 fault. When the borehole had been completed Ickes thought that it passed through this fault at between 1350 and 1550 feet; this, he says, would give the fault a hade of 60°, and would cause it to strike the limestone about 1000 ft. to the E. of the well. This view, which has been accepted by others, was, however, based on the log of one well only. It is almost certain that it would have been modified if the information obtained from the two later

wells had been available. It certainly does not account for the logged position of the Kilburn and lower coal seams in the three boreholes and the depth at which the top of the limestone occurs in No. 3. Moreover, such a view leaves us to find ingenious explanations to account for the oil found in the limestone in No. 1 and the salt water found in No. 2.

VII. Water Conditions in the Boreholes.

The water conditions near the top of the Mountain Limestone provide an interesting study and throw some light on this question of faulting. In Bore No. 1 the limestone was penetrated to a depth of 53 ft. without finding water. In No. 2 a bed of sand, at least 60 ft. thick, was found 75 ft. below the top of the limestone. From this sand there was a strong flow of salt water which kept a constant head of 2800 ft. which could not be lowered by bailing. No. 3 penetrated to a depth of nearly 800 ft. below the limestone but only found a negligible quantity of water in volcanic ash 200 ft. below the top. Water broke in at the bottom of No. 1 some time after completion. It has been supposed that it may be coming from a leak in the casing and that it is coming from a water sand at the base of the Coal Measures logged at 1515 ft. This water was never analysed, so this supposition can not be checked. The waters coming in at the bottom in both No. 1 and No. 2 wells were analysed and the results given on page 365 seem to indicate that both are limestone waters, so that water may have broken in through fissures in the limestone in No. 1. If so the waters are coming from different sources for they are quite different in character, the analyst stating that " this water (No. 2) contains twice as much mineral matter in solution and the Alkaline Chlorides are 2½ times as great " (as in No. 1). We, therefore, have evidence from the limestone waters confirming the supposition that a water-tight fault must exist somewhere between the bottom of Bore No. 2 and Bore No. 3. It is possible to explain the conditions found in No. 1 by assuming either that the bottom water is due to leaky casing above or that the water sand in No. 2 is lenticular and thins out within a distance of the 1200 ft. which separates this borehole from No. 3, but it is difficult to imagine that such a body of water would not find its way through the limestones into the other wells. A fault throwing down 150 ft. of shales against the limestone to the E. of No. 2 is the simplest explanation of all the facts.

VIII. Petroleum Accumulation at Hardstoft.

The foregoing study of the faulting and water conditions is an important preliminary to the examination of the occur-

rence of petroleum in these bores. Numerous shows of oil and gas were met with in drilling these wells, some of them being large enough to afford samples of several gallons each. The analysis of these samples, when compared with those of the main supply found in No. 1 bore, show a generic similarity in spite of differences in the percentages of constituent fractions. This fact, together with the fact that in very many instances showings of oil are met with in coal workings all over this North-Midland Coalfield area in close proximity to faults, has led to attempts to trace the faults across the boreholes by means of the oil showings. I do not think that any reliable results can be so obtained. I do not doubt that the faults have lent themselves to the migration of oil to higher levels though it has been urged that it is difficult to see how such migration could take place along fracture planes which involved large masses of shaley and clayey strata. I think the difficulty in such cases lies in envisaging the enormous time factor involved. These displacements in the strata were not completed in a moment even of geological time. Water may have been able to percolate slowly along them at some periods in their history and not at others, and any such percolation would involve the passage of any oil present along with the water. If such migrating water found its way into a porous stratum so would the oil along with it and it might percolate to considerable distances from its point or plane of access. Thus the oil which is showing may have been originally connected with a fault but may at present lie at a considerable distance from it. Any subsequent disturbance of the strata by folding or faulting or any circumstance which would lead to water movements in the beds would also bring about changes in the position of the oil.

Coming now to the problem of the oil supply in the No. 1 bore. I think it is certain that it is trapped against a fault which passes to the E. of it, most probably the No. 2 fault. There are fewer difficulties if we consider it to cut the Mountain Limestone very near to the eastern side of the borehole. Such a fault would bring Limestone Shales against the limestone to the E. and prevent an extension of the oil accumulation towards Bore No. 3. This accumulation must lie against the fault and probably along it in an irregular way, but it can not have any considerable extension to the W. The top of the limestone is higher in the No. 1 well than in No. 2 so that the accumulation is found where we should expect it. Traces of oil were found at the same horizon in No. 2 and a very little oil came in with the underlying water showing that the liquid had found its way in this direction, whereas nothing was found in this position in No. 3 showing that some effective seal exists to the E. of No. 1.

IX. The Origin of the Oil.

Seepages, drippings and even small flows of petroleum are very frequently met with in the coalfields that lie around the southern end of the Pennines. New occurrences are reported every year and almost invariably in association with fault planes. The oils are so similar in character to that found at Hardstoft that there has been some tendency to look for the origin of the oil in the coal measures. But though there is no difficulty in accounting for upward or even lateral migration of petroleum it is difficult to imagine migration to beds below, especially through shales and waterlogged strata. Graham and Skinner[7] have endeavoured "to throw light on the mode of formation of these occasional drippings" and to "ascertain how far the composition and properties of the oils found naturally compare with those of oils obtained by the destructive distillation of various carbonaceous materials at the lowest temperature at which decomposition is found to take place with the production of oil in appreciable quantity." The authors had in mind that geological disturbances, such as faults, might produce temperatures capable of resulting in distillation of carbonaceous material. The authors were able to prove as a result of their investigations "that the natural oil . . . owes its existence to causes other than destructive distillation of carbonaceous material." In other words the oil is quite independent of the coal so far as its source of origin is concerned.

Looking into the question in connection with the Carbon Ratio Theory* I find from the analyses available to me that the Carbon Ratios of coals taken from seams worked in the Derbyshire field run between 63·5 and 70. Such ratios are found in connection with gas and traces of light oil by the theorists. It looks as though the theory works very well in this area. It is sometimes objected that the Carbon Ratio theory is unscientific. So are many theories in science. The only pertinent question that need be asked is "Does the theory work?" It does work very well in many observed cases and what is more important to myself is that it has worked in cases where I have been able to use it in the field. If we may draw any conclusion from the application of the theory it is that we must look for the source of origin of the oil elsewhere than in the Coal Measures, which agrees with the conclusion arrived at on other grounds.

Bromehead[3] after classifying petroleums as:

(1) Those with a paraffin base indigenous to shales,

(2) Those with an asphaltic base indigenous to limestones,

comes to the conclusion that the petroleum at Hardstoft originated

* See Dr. Murray Stuart's paper on "Carbon Ratios," *J. Inst. Petr. Techn.*, 1927, **13** (61), 308–310.

in the lower part of the Limestone Shales (Yoredales) "which" he says, "are black in colour and of an 'oily' appearance and occasionally show little veins of black bitumen in the bedding." While I hesitate to accept his classification of the petroleums as being completely established there is much to be said in its favour. Observers have noted for well over a hundred years many instances in the area around the Peak of the occurrence of petroleum near the junction between the base of the Limestone Shales and the underlying Mountain Limestones. A true oil-shale was met with well up in the Limestone Shales in Bore No. 1 and gas was found low in the shales in No. 2. Moreover, Bromehead's theory would fit in well with the actual circumstances in which the oil is found in the No. 1 well. Against the theory is the fact that in one of the wells drilled by the Government, Ironville No. 1, the Mountain Limestone was, accordingly to Giffard (4, p. 17) struck at 1600 ft. and a good show of thick, heavy oil met with at 2031 ft. and smaller quantities of oil found at 2500 ft. and 3604 ft. respectively. Unless some very considerable faulting takes place in the neighbourhood it is difficult to connect occurrences of oil extending to a depth of 2000 ft. in the limestone with the Limestone Shales. Giffard (p. 25) therefore says, "It is conceivable that the oil may be ascending the fault plane from greater depths and the possibility of the oil being of Devonian origin is one that must not be lost sight of."

If, however, in this locality, the Mountain Limestone happens to be unusually free from water, it is possible to consider that the oil from the overlying shales may have migrated downwards through joints and fissures. The bore at Ironville is situated on a very well marked dome structure. It is interesting to note that the Riddings Colliery, in which the flow of oil occurred which so interested Dr. James Young in 1847 and which led to the development of the Oil Shale Industry in Scotland, is on this structure. Such folding in the limestones connotes a good deal of jointing and fissuring through which the oil might very well seep to lower horizons. Against this, however, is the fact that at 3500 ft., or over 100 ft. above the lowest depth at which oil was met with, very large quantities of salt water were found in the limestone, which seems to dispose of any theory of downward migration of the oil.

But for the occurrences in the Ironville borehole I should be inclined to accept Bromehead's theory. I have seen no analysis of the heavy oil found at Ironville, and it may be that is of a different character from that obtained in Hardstoft No. 1 and, therefore, quite independent of it. However, the only conclusion possible on the evidence available is that the oil is apparently of very deep seated origin and that it reaches porous strata at higher levels by migrating along fault planes.

X. *Future Prospects.*

To come to the conclusion that the first bore to be commenced under the Government scheme for the purpose of seeking for oil in England, struck the only large supply that exists, or can possibly exist, would be absurd. Such a borehole is but a pinprick on the surface of the country and to imagine that such a pinprick discovered all that is to be found in the length and breadth of only the Northern Midlands would be to imagine a vain set of improbabilities. If my reasonings are correct it is almost certain that more oil is to be obtained, possibly in larger quantities than those already yielded by No. 1 Hardstoft, along the same fault plane and at the same horizon. There is no reason to doubt that similar accumulations exist in favourable situations elsewhere. Dr. Veatch[2], who is a petroleum geologist of the highest standing, states (p. 7) that "the petroleum possibilities of the Midlands of England were of a most amazing and striking character." In spite of the failure of the Government test borings both Veatch and Ickes think that profitable oilfield areas can be discovered. Ickes[1] says that "the writing off of the expenditure already incurred as a loss is premature," and considers that more work should be done. After all, the number of test bores which have been completed are nothing at all as compared with the numbers put down annually by American companies, and the number of dry holes drilled in America as compared with the successful ones is still greater than the 13 to 1 result experienced here. It may be that we are only beginning to learn how to select drilling sites which have a chance of being successful in the Midland area. Evidently there is a great deal more to be learned in this connection. What of the areas to East and West where the Coal Measures lie concealed beneath the newer rocks? A 13-ft. oil sand was found in the Millstone Grits in the Kelham borehole, and another 10-ft. thick in the Coal Measures in the borehole at Retford. The oil found in both cases was similar in character. Possibly in neither case was the structure favourable to accumulation in quantity but such sands suggest profitable accumulation of petroleum under good structural conditions. Ickes also notes the occurrence of an outcropping oil-sand of Triassic age 30-ft. thick at Burton, 12 miles S. of Derby. He found that on treating this sand by solvents, 2½ per cent. of petroleum could be extracted, and that the oil had similar characteristics to those found lower down in the Carboniferous strata in Derbyshire.

It appears to be certain, therefore, that accumulations of petroleum possibly of comparatively large dimensions remain to be discovered in England. The main problem is whether it will

be a profitable business to seek for such accumulations and this, at present, is where doubts arise. In the first place our optimism must be largely based upon the results obtained in Hardstoft No. 1, and this is rather an unsatisfactory basis. If the oil accumulation there had been a simple oil pool associated with a normal structure it would have given much more confidence. Many good structures were drilled and were found to be barren from a commercial point of view. Seeking for oil accumulations against faults is much too complicated and risky a business to be undertaken for commercial purposes at present. Moreover, I do not think that any concern could be persuaded to spend the very considerable amount of money that would be required in endeavouring to find suitable structures on the oil sands found at Kelham and Retford. In America these things are done because experience has taught the operator that, given certain conditions, he is very likely to find petroleum in large quantities and that in consequence his profits are very large indeed. In this country the little experience we have suggests failure as the result of our search rather than anything else. Thus there are difficulties in the way of a commercial search for oil in England which are in part practical and, in part, psychological. Further difficulties come to light when we look into the question of obtaining leases upon land for the purpose of drilling. We may dismiss the possibility of obtaining prospecting leases over large areas as out of the question altogether. Where land is minutely subdivided as it is in some parts of the Midlands, it is a complicated and almost impossible task to block up an area such as a company would require for drilling purposes. Veatch[2] spent some time in looking into this question and states (p. 3) that in the case of one large estate, the principal revenues of which are from coal leases, the average time between the agreement on terms for a coal lease and the signing of the contract has been 8 years. In another case which came to his knowledge, although the terms for a coal lease had been agreed upon 15 years previously, the contract was still unsigned. It is quite likely that matters would be more difficult and prolonged with regard to leases for oil well drilling, for there are practically no precedents to go upon. No company could go on if such delays were encountered. Again, it is unfortunate from the point of view of the seeker for petroleum that the most favourable areas we know of at present lie in important coalfield areas and are, therefore, largely under the influence of the coal mining interests. American investigators did not find these interests too friendly and, in the present circumstances, powerful opposition to any attempt to prospect for fuel resources of a competitive character could quite naturally be expected in this quarter. Finally, if we assume that a lease has

been obtained against every obstacle, we have to consider what must happen should the borehole pass through coal seams. At Hardstoft a pillar of coal 2½ acres in extent had to be left around the bore where it passed through the seam, and the coal owner had to be compensated for the loss of this coal. Consider a borehole likely to pass through three or four such seams, with an average thickness of, say, only 3 ft. The sum that would have to be paid out in compensation for what amounts to nearly 30,000 tons of coal at least is sufficiently great to cast a cold douche over any optimistic seeker for oil, especially when the other risks attaching to his venture are considered.

The conclusions I come to at the end of this chapter are that although I am sure that accumulations of oil do exist in the Midlands of England, I am also quite sure that to look for them is not at present a commercial proposition. Some day either when there is a dearth of fuels or in some case of national emergency the search for oil in England may be commenced again.

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NOTE.—These papers are referred to by numbers in the text.

DISCUSSION.

Dr. J. A. L. Henderson, in opening the discussion, thought the Paper was of general interest in that it brought the information relating to the oil occurrence and drilling at Hardstoft up-to-date. The last two wells bored, Nos. 2 and 3, had yielded surprising results and information which had proved decisive in certain directions. He regretted, however, that the diagrams and photographs the author had shown on the screen were not available previous to the reading of the Paper, because so much depended upon certain structures which were therein depicted. He had

been responsible for the selection of the site and the drilling of No. 2 well. In this connexion it was necessary to bear in mind that the choice of drilling sites on any possibly favourable structure, in Derbyshire and other parts of the Midlands, was severely restricted by the necessity of avoiding any interference with or possible damage to the coal workings. The production of coal was the most important industry in that particular part of the country. Therefore, although one might have preferred other locations for test borings, there were only small areas available within which the choice could be made. He agreed with Dr. Wade that the borings had shown that the oil in that part of Derbyshire, particularly within the Hardstoft dome, was associated with faulting. The author had in his Paper reviewed generally the history of previous investigations and the conclusions of a number of authorities on the subject of the occurrence of oil in England. In 1917, after investigating the subject on the spot, he definitely came to the conclusion that the areas which had been described that evening within which the test bores had subsequently been made, represented what might be called the disturbed foothills of the Pennines, which one would avoid in ordinary test drilling practice. They nevertheless yielded abundant indications of petroleum and were worth testing even for geological information and guidance. He had expressed his opinion that if oil were present in quantity within the Midlands it would probably be found concentrated in areas of less disturbance and more gentle folding—*i.e.*, to the north-east and east of the large structure of the Pennine Range, within the region covered by the most valuable coalfields in the country. He subsequently made a very careful investigation of the feasibility of testing economically the oil possibilities of certain parts of both England and Scotland; and he came to the conclusion that, unless developed and worked by the owner of all minerals, no oilfield, located within the coal-bearing areas, unless it yielded enormous quantities of petroleum, could possibly pay because of the very heavy charges which would rightly have to be faced. An oil industry would undoubtedly be secondary to the coal industry in this country. Coal was of first importance, and that was where the damages which had to be taken into consideration first began. There were first of all the underground damages; it was necessary to guard against ingress of water, oil and gas; there was the need for supports or pillars; and then it was necessary to protect the fire clay, iron ore and other interests. Towards the surface limestone quarries, building stone quarries, the sand and the gravel pits had to be considered; while on the surface consideration had to be paid to the riparian rights, pollution of drinking water and surface damages. Rental of the well sites, damages and way leaves for

pipe-lines, paths, roads to wells, tank sites and settling pits are also, almost of necessity, very high in this country in comparison with those prevailing in the chief oil-producing countries. Serious consideration also had to be paid to the questions of royalties, high taxation and rates, the incidence of labour legislation, and the high railway freightage for crude oil and its products compared with the United States and Canada. As a consequence of the safeguards demanded in drilling, the cost of deep wells would be excessive. For instance, much heavy casing of various sizes is required: cementing must be done most carefully and frequently in order to shut off all water, gas and oil from coal seams, from other minerals, and from faults. Taking all these factors into consideration, and summing up the whole situation, he came to the conclusion that even if oil were proved in quantity within or beneath the Coal Measures, its exploitation would be unprofitable. The disadvantage would largely disappear in the case of petroleum-bearing areas which might exist where other valuable minerals were not present, but in regard to any such he had no personal knowledge.

In the latter part of his Paper the author had raised what he considered was the most important point from the results of the borings, because the cumulative evidence obtained in Derbyshire seemed to point to a deeper-seated source of the oil—*i.e.*, either within the Carboniferous Limestone series or beneath it. Dr. Wade had not referred to one subject with which he hoped he would have dealt, namely, the possibility and probability of lateral variation of the sediments in the Carboniferous Limestone series. Unexpected sandstones and shales had been intersected in the boreholes at or near the top of that series, and it would be interesting if the author had obtained further evidence on the subject, which might throw some light upon the possibility of finding oil reservoirs within the series. Nobody knew, as far as he could ascertain, what the character of the sediments towards the base of the Carboniferous Limestone in Derbyshire was; and that was one of the most important points that had to be borne in mind in that connexion.

The production record of the Hardstoft No. 1 well was very interesting. He thought it was better in this case, in view of its history, to judge the character and prospects of the well from its recorded natural flow, rather than from its erratic pumping results. The high peak of production obtained in 1924 was to be expected. It represented the transition from the long-sustained flowing period, to production by pumping, after cleaning the well of its accumulation of wax, sand, shale and a water column of almost 1,600 ft. The most marked characteristic was the extraordinary persistence of oil flow during the first flowing period of over four and a half

years against a column of oil and water exceeding 3,000 ft., and in spite of lack of proper attention and cleaning. In 1926, no less than eight years after bringing into production, it was yielding, according to a test, by natural flow, at the rate of 26 per cent. of its initial average flow,—a remarkable result. That indicated long life, with a relatively small pumping production which might persist in the ordinary course for another fifteen years to what would in large fields be the economic limit. The whole question of economics had to be borne in mind in connection with the question. Where one barrel a day would pay with a thousand wells, it would not pay with one well. The economic limit which could be applied to Hardstoft was not the economic limit which was applied to other fields of a similar class. There was, however, the record of a production of almost 20,000 barrels of high grade oil with remarkable persistence of flow, and he understood that the oil was still as highly charged with gas as at the beginning of the well's history. These facts pointed to some very considerable source of supply, and led one to believe that if it were only possible to continue the investigations a large deep-seated source might be found. The successful prosecution of such a project, however, was, he was afraid, out of the question. He hoped, in conclusion, that some of the members who had studied the geological side of the question in particular would give the Institution the benefit of their views.

Mr. E. H. Cunningham Craig thought the members were very much indebted to the author for giving such a clear and comprehensive account of an occurrence of oil which had puzzled a great many people. After what Dr. Wade had said, he did not think there could be much doubt about how the oil was trapped in that area, and there could be little doubt either where it came from. It had come a considerable distance and it showed certain remarkable characteristics of filtered oils. He did not wish to speak about Hardstoft oil, because the author in his Paper had opened up a very much larger subject—*i.e.*, whether it was possible to find petroleum in this country. That was a subject to which he (Mr. Cunningham Craig) had given a great deal of attention even before the war. In 1916 he reported upon the possibilities of obtaining petroleum in Scotland. At that time he went so far, after giving all the evidence of the well-known occurrences of free petroleum in that country as distinguished from the petroleum formed by natural distillation from oil shales by the heat of igneous intrusions, as to suggest that one of the domes in the oil shale field should be tested, and also the great anticline which was known as the Cousland Darcy anticline just outside the oil shale field; and he actually went so far as to locate on the six-inch maps two sites for bores. In the following year, when word went out from the highest

quarters that petroleum must be obtained in any possible way in this country regardless of expense, he turned his attention to the possible chances in England. At that time Dr. Henderson and he were associated under the late Sir Boverton Redwood in the Petroleum Research Department. One of the first regions to which he very naturally turned was the Pennine Chain and its two flanks. The chain of little domes on the flanks was known to him because he had had occasion to study the earlier movement which had taken place which, combined with the second great movement, had formed those domes. The fact of those two movements one upon the other caused those faults which had been shown so clearly in the diagrams that had been exhibited. He had had occasion to deal with the earlier movement not in connection with oil but in connection with certain coals; and it was quite evident, when he studied the subject carefully, that on those domes, and especially on the lines of the earlier movement, slight accumulations of oil were found. He made a selection of three areas, but he did not choose Hardstoft for two reasons: firstly, because it seemed rather a small dome and that bigger ones could be obtained in the neighbourhood; and secondly, on account of the faults. He desired in the next place to join issue with the author on one particular point. Dr. Wade stated at the beginning of his Paper that the Hardstoft well was the only well that ever looked like being a commercial proposition. He disagreed with that statement because he thought that the well at Darcy was from the start a much better proposition than the Hardstoft one. The well at Darcy was drilled within 20 ft. of the spot he marked upon the six-inch maps. He had studied the very carefully compiled data published by the Geological Survey of Scotland and was very much interested in its progress; but he would have preferred the location of the well to have been at Cousland. The well was drilled where it did not have to go through any coal seams. There were slight faults down the flanks of the structure, but it was a very much larger structure than any of the little domes on the flanks of the Pennines, and on the whole a much better structure in regard to dips and size of concentration area. It was not a case of drilling blindly to find oil wherever it might happen to be. There were four sandstones well known in Scotland, of which the uppermost two, at any rate, were known to be oil bearing and to contain residues and remains of oil in numerous places; and the two lower sandstones certainly gave evidence of having been at one time oil-bearing. It was possible to calculate the depths at which those sandstones would be found, but it was necessary to allow for a good deal of variation as there was a thinning out of the series towards the south-east. Having deducted about 300 ft. for

that thinning he was able to estimate that the first possible horizon would be at about 1,500 ft.; the second at about 1,800 ft.; the third at about 2,600 ft.; and the fourth at about 2,900 ft. There was a slight show of oil at quite a shallow depth. The first really good show was at 1,490 ft.; the second one, where a certain amount of oil was struck, was at 1,810 ft. The well was never continued. No really good attempt was made to produce the oil at that depth, and the two lower horizons had never been tested yet. He thought that in the structure that there existed there was really a chance of striking oil in reasonable quantity. The oil that was produced was naturally very waxy. It was highly inspissated; on a cold day it was quite solid. It occurred in a hard calcareous sandstone, the upper part of which was found to be filled with little soft blebs of wax. As he had previously said, the well had never really been produced properly, and it was abandoned at a depth of about 1,812 ft. It seemed to him that a possibility existed there, without incurring very great expense, of testing a very promising structure. Unfortunately, he was not able to recommend it as a commercial proposition to the company which asked him to look into the matter, for several reasons, the price that was asked for it being one, another being the reason to which both the author and Dr. Henderson had referred, the difficulty of making arrangements with the proprietors. There might be other places in England where it was worth while to put down a well, but he was afraid there were not very many. He had had the pleasure of discussing the subject over and over again with Dr. Veatch, who was always more confident than he (Mr. Cunningham Craig) was in regard to the striking of oil because he (Mr. Cunningham Craig) looked, perhaps, more to two or three horizons in the millstone grit, and when those horizons only produced a little heavy oil and a good deal of gas it was borne in upon him that the oilfields of England were, at any rate to a great extent, "have beens." Oil had existed there probably in considerable quantities. There were filtered residues in the more close-grained rocks in the neighbourhood, but there was nothing now left but slight signs, shows, heavy inspissated oil in places and occasionally a good deal of gas. He was afraid, therefore, he must associate himself with the somewhat pessimistic remarks of Dr. Henderson. The subject, however, was one of very great interest, and there was no saying whether in concealed structures they might yet find a locality in which the oil had still been preserved.

Mr. J. L. Jeffery said he had listened with much interest to Dr. Wade's instructive paper, and there seemed to be one or two doubtful points in connection with the figures which required elucidation. The first one was the depth at which oil was struck

in the Hardstoft No. 1 well. It was actually at 3,075 ft., not 3,070 ft., which made a difference in certain of the calculations. The question of the thickness of the oil sand also came in. He happened to be on the spot when the oil was actually struck. The boring went through hard "shell" for about six inches or a foot, and then there were 2 ft. of oil sand. After that the drill entered a fairly hard limestone; it was pushed forward to about 3,130 ft., and after that it entered very solid limestone. That also indicated the reason why no water was struck if the well was plotted in comparison with No. 2 well where water was found. The heavy water struck in No. 2 well was found a good 30 or 40 ft. below where the drill actually stopped working in No. 1 well; so that there was no doubt, he thought, that the water which was now finding its way into the well was not from below but must be coming down from the back of the casing or through some faulty joint in the 8-inch-casing further up. He noticed that a question was also raised with regard to perforations in the 6¾-inch lining. A 6¾-inch liner was put into the well, but unfortunately the drillers dropped it when lowering it, and they were not quite certain where it landed. Nevertheless, it did not stop the well from producing and it went on very satisfactorily. With regard to the production from the well in the first few months—*i.e.*, from May 27th, 1919, to the end of the year, the figure given by Mr. Ickes of 1,666 U.S. barrels was approximately correct: it should be 1,674 barrels. He had no doubt that a discrepancy had crept in through an endeavour having been made to calculate out what the production would have been in the year. As a matter of fact, it was only actually producing for 7 months. The well came in on its natural flow; it was not pumped for the first year or so; and it was put on a test in 1921, he believed. He had not the figures with him because he did not know the details that the paper would refer to, and he was, therefore, speaking largely from memory. In 1920 or 1921 it was decided to ascertain what the production capacity of the well was, and it was put on pumping for about 3 months. That probably did the well no good because afterwards it was allowed to stand again and it naturally got waxed up. That accounted for the low production in 1922, as the author rightly surmised. The Government was in rather an awkward position about that time, because it did not know to whom the oil belonged. Certain questions were raised into which it was unnecessary to enter at the present moment; but the well was then taken over by the Duke of Devonshire and proper operations started in 1924. It was not desired to produce a lot of oil at that time because there were no means of storing it, and any marketing of it had to be done under trust, so to speak. The Government was not altogether to blame for that. Besides that,

the boring during the war was let out under contract to Lord Cowdray's firm. They were the contractors for the Government and therefore kept the logs and obtained all the information; and Mr. Ickes as their representative was the only source from which information was available at that time. Of course the Government had access to that information, but there was certain information that other people were not able to obtain at the time. There were a few other points in regard to which he desired to ask the author some questions. As near as anything the total production of Hardstoft No. 1 well up to date was 18,500 barrels, which amounted to about 2,400 tons, there being 7.75 barrels to the ton. It was rather interesting to observe that the sand was only 2 ft. thick and that all that oil must have come from an area of 180,000 sq. ft. or approximately 4 acres; or a radius from the well of 250 ft., presuming that 75 per cent. of the oil was left in the ground, which was according to American practice in reckoning extraction from oil sand. The nearest wells were 600 ft. away, but it seemed extraordinary that if all the oil came from that small piece of sand it should come so far. The question was certainly worth considering where the oil did come from. There was a little doubt in his mind as to the top of the limestone in well No. 3. He did not see the samples then because he had nothing to do with the well, but it was not easy to determine the mountain limestone in that area on account of numerous shale and sand beds being interlaminated between the mountain limestone proper, especially in the upper part of it where it came in contact with the limestone shale. It was possible to understand this from the way the sediments were formed, and it was possible to recognise them if the boring was watched very closely at the time that the sands came out. He rather thought that the horizon had been taken too low as being the top of the mountain limestone. Another significant fact which had been largely overlooked was that, with the exception of the Brimington well, very marked traces of oil were found in all the wells at the same horizon at which the No. 1 Hardstoft well came in. That also applied to Ironville No. 1, which Dr. Wade had mentioned. Ironville No. 1 had several shows of oil; in particular a strong show was found at the Hardstoft horizon—*i.e.*, between the limestone shale and the top of the mountain limestone. The shows of oil in the carboniferous limestone which were entered for a distance of 1,600 ft. were found practically the whole way down—very small shows, many of them only to be obtained by leeching with ether or carbon di-sulphide; but nevertheless it showed that the limestone was more or less petroliferous, and this was true over most of Derbyshire. There were some very thick dolomite beds in Derbyshire occurring, especially in the lower

parts of the limestone, which might possibly be a source of the oil. With regard to the Darcy well which Mr. Cunningham Craig had mentioned, it rather looked as though the Government had been foolish enough to abandon a well just as it was getting to an interesting stage. There were certain engineering difficulties which caused that well to be abandoned; indeed, all the operations were eventually brought to an end about that time. The casing had to be withdrawn six or seven times due to the sliding of the upper strata and some loose boulders which kept on pushing the well out of the vertical, thus causing an enormous amount of trouble. It was only with the greatest difficulty that the drillers were able to get down to 1,800 ft., where the show of oil was struck. It was very desirable to go further, and the drillers themselves would have liked to prove the sand properly. It was not possible to prove that sand, and afterwards the whole work had to be stopped because it was useless to try and go on with the well. A new well would have had to be drilled, and that would simply have meant throwing good money after bad.

Mr. A. MacDougall said that Mr. Cunningham Craig had stated that, generally speaking, the oil in Great Britain was a filtrate. If he was right in assuming that to be Mr. Cunningham Craig's view he desired to ask him in what direction it had gone or the direction in which it was likely to be found.

Mr. C. B. Roach said the author had shown a picture of what he termed an oil show or a sort of dry bitumen in Derbyshire. He desired to ask whether the author thought that was a real bitumen show or the elaterite which occurred in that region. He agreed with the remarks Mr. Cunningham Craig had made in regard to the occurrence of oil in England in commercial quantities. He noted with interest that the oil of Carboniferous age obtained from the Hardstoft well was similar to the Pennsylvanian crude oil. In Pennsylvania the Carboniferous rocks were practically horizontal and as undisturbed as beds of such great age can possibly be. But when getting near to the Appalachian Mountains, with dips of 5 degrees and 10 degrees, there was no oil on any commercial scale. The same thing could be applied in England, but all the beds were very much disturbed compared with those in Pennsylvania and the Mid-Continent. The oil at Hardstoft, therefore, could only be accidentally preserved since there was too much faulting in the region, and also the surface dips were as much as 5 degrees. In any case the area of the Hardstoft dome was a very small one.

The President said that it had been very interesting to hear what the author had to say on the question of future prospects with regard to the incidence of oil in England. As he understood it the author was sure that accumulations of oil existed in the

Midlands of England, but he was equally sure that it would not be a commercial proposition to look for such deposits; and the various speakers who had taken part in the discussion had indicated their agreement with the author's view. Personally, he was rather sceptical on the subject himself in view of the fact that so little encouragement had been obtained in the search for oil in England, whether in the case of a national emergency, when the question of expense was taken out of the commercial orbit, or otherwise. He was a little doubtful whether the Government, with so little encouragement, would again spend a very great deal of time and money in looking for oils, although Dr. Wade was quite sure that considerable deposits existed in the Midlands. At any rate, he thought the members would agree with the author that in a country such as the Midlands, which was very largely industrialised and where the land was split up into comparatively small holdings, it was a totally different proposition from prospecting for oil in other places, where the area was so much more widely spread; and that it would be almost impossible to attempt to find the money as a commercial proposition to carry on drilling operations under the conditions. He was sure it would be the desire of the members to accord a most hearty vote of thanks to Dr. Wade for the very valuable contribution he had made to the records of the Institution.

The resolution of thanks was carried with acclamation.

Dr. Arthur Wade, in reply, said that most of the members were interested in the question of oil in England, and to himself it was a most intriguing and fascinating problem. He was very much obliged to the various speakers for the information they had given, and he agreed with most of the points they had raised. The main question that Dr. Henderson asked was with regard to the possibility of lateral variations in sediments such as sandstones and shales which were found in the upper part of the Carboniferous Limestones. He had given some time to the consideration of that subject, but he was afraid he had not sufficient information to justify publication. In considering what underlay the Carboniferous Limestone in Derbyshire there was evidence of some interesting possibilities. The lateral variation in the sediments was an interesting problem, and there was no doubt that it might play an important part in connection with the question of petroleum in the Midlands. He agreed with Mr. Cunningham Craig in his references to the Darcy well, although apparently in the Paper he did not. As a matter of fact, Mr. Cunningham Craig and himself were talking of two different things, *i.e.*, what had actually been produced from the Darcy well and what the Darcy well might have produced had it been drilled to greater depth. The Darcy well might have been a good well if it had

been carried deeper, although, as Mr. Jeffery said, engineering difficulties had to be faced. He was much obliged to Mr. Jeffery for correcting some of the figures with regard to the Hardstoft well. With regard to depth at which the top of the limestone occurred in No. 3 well, he agreed with Mr. Jeffery that there must be some doubt as to the exact figure, but there was no doubt that it was a good deal lower than in No. 1 well. He thought that Mr. Cunningham Craig had better answer Mr. MacDougall's question as to where the oil in England had gone. Mr. Roach had raised a question with regard to the seepage at Castleton. Many occurrences of petroleum had been recorded in Derbyshire at about the same horizon—about the junction of the limestone with the overlying limestone shales, and he was inclined to connect them both with regard to nature and origin. Mr. Roach had further raised the question of dip in connection with accumulations of oil and stated that in Pennsylvania oil occurred in beds which were almost horizontal. There were fields in America where the dips were at any rate equal to those which were observed in the Derbyshire areas. He agreed with Mr. Roach that the dome at Hardstoft was of a small size. Even if it were unfaulted and it was an area of ordinary accumulation it probably would not have produced oil in similar quantities to those obtained in some of the big domes observed in the United States. At the same time he had seen domes not very much bigger than the Hardstoft dome produce quite large supplies of oil where they were favourably situated in oil-bearing countries. On the other hand, one liked to have a large area of accumulation. There was certainly a connection between area of accumulation and the quantity of oil produced. In the present instance it was necessary to take faults into consideration. It was not a simple question of accumulation in a dome structure, but the oil may be migrating along a fault from a deeper source of supply and was found at the top of the limestone because it had been trapped there by overlying and adjacent shales.

The meeting then terminated.

During the month of April, 1928, and since the reading of the foregoing Paper, No. 1 Hardstoft has commenced to flow again over the top of the casing of its own accord. The well had been shut down for a time for repairs to the sucker rods.

This is, I think, the most remarkable thing which has happened in connection with a most remarkable oil well. It seems to support the theory that the oil must be coming from some deep-seated source of supply, which is of considerable magnitude and under great pressure. It also confirms the belief that more oil must exist in these Midland areas than has been supposed.—A. W.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND ELEVENTH GENERAL MEETING of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, W.C. 2, on Tuesday, April 17, 1928, at 8.30 p.m. In the absence of the President the chair was taken by Dr. A. E. Dunstan, Vice-President.

THE CHAIRMAN said he had to apologise for the absence of the President, who was prevented by ill-health from attending.

He had one very pleasant fact to announce—namely, that that afternoon the Institution had secured its third branch in Trinidad. There were now three branches of the Institution established overseas, there being branches—in order of formation—in Rumania, Persia and Trinidad. There was every hope of adding to that list in the near future.

There was no need for him to introduce the reader of the paper, Mr. C. H. S. Edmonds. Mr. Edmonds was a member of the Institution and a distinguished member of various American societies. He was a recognised expert on his subject, and the members would listen with great interest and pleasure to what he had to say on the subject of modern developments in tube-still distillation.

Tube-Still Distillation.

BY C. H. S. EDMONDS, M.Am.Soc.Mech.E., M.Am.Pet.Inst. (Member).

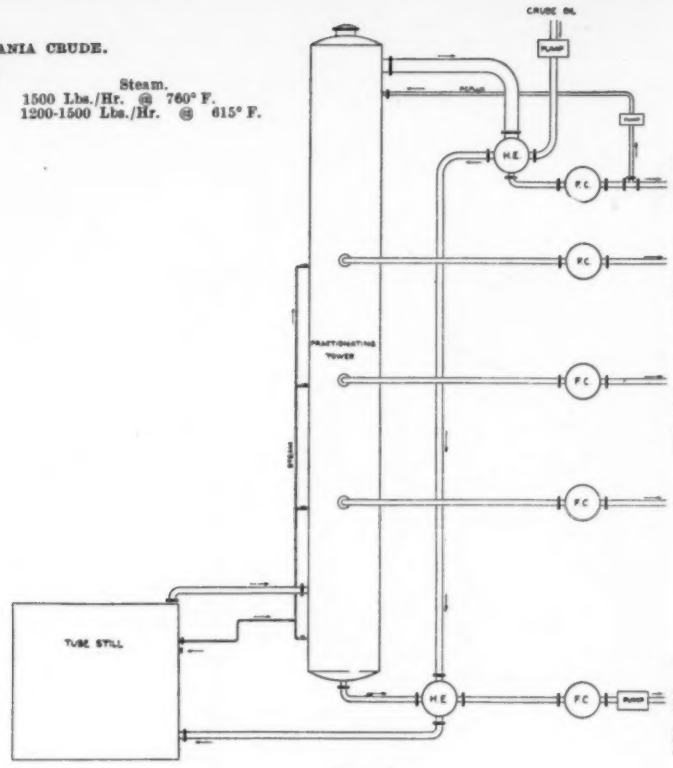
THE distillation of crude oil constitutes the most important refining operation, and the past few years have witnessed very definite developments in the type of equipment installed for this purpose.

The shell still used either as a batch unit or as a continuous battery and fitted with more or less efficient fractionating equipment, is giving place to the modern tube still and positive type bubble tower yielding products of definite specifications in one operation, thus reducing substantially the amount of re-running and permitting relatively lower manufacturing costs for investment in equipment, direct fuel, process steam and loss of material. Quite naturally, during such development, there have been difficulties to overcome, but the refining industry may be permitted to congratulate itself that progress in its technical methods will bear comparison with other major industries.

The refiner demands distilling equipment that possesses flexibility to take full advantage of different crude oils and varying market conditions and demand for products, and obviously such flexibility must at times be secured at some loss of commercial efficiency.

PENNSYLVANIA CRUDE.

	Throughput.	Tube Still Outlet.	Steam.
No. 1.	2000 Bbls.P.D.	780° F.	1500 Lbs./Hr. @ 760° F.
No. 2.	2200 Bbls.P.D.	600° F.	1200-1500 Lbs./Hr. @ 615° F.



No. 1		No. 2	
Gasoline	38-39%.	Gasoline	39-40%.
Gravity	59° A.P.I.	Gravity	58·8° A.P.I.
90%	392° F.	90%	398° F.
E.P.	424° F.	E.P.	428° F.

Cracking Stock	18-20%.	Kerosine	4-5%.
Gravity	40·5° A.P.I.	Gravity	43·5° A.P.I.
I.B.P.	450° F.	I.B.P.	430° F.
E.P.	580° F.	E.P.	505° F.
Flash	220° F.	Flash	205° F.

Wax Distillate	19-20%.	Gas Oil	24-26%.
Gravity	33·2° A.P.I.	Gravity	36·0° A.P.I.
80-85 Viscosity @ 100° F.		I.B.P.	528° F.
Flash	315° F.	12%	550° F.
Pour	75° F.		

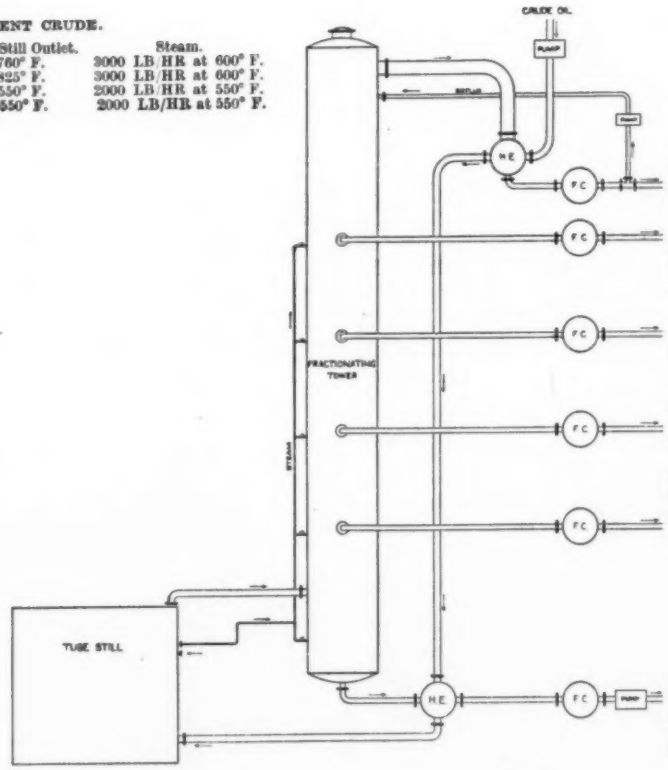
Wax Slop 6-8%.

Cylinder Stock	13-15%.	Long Residuum	29-30%.
Gravity	23·8° A.P.I.	Gravity	27·2° A.P.I.
235 Viscosity @ 210° F.		Flash	450° F.
Flash	610° F.	Fire	520° F.
Fire	680° F.		

FIG. 1.

MID-CONTINENT CRUDE.

	Throughput.	Tube Still Outlet.	Steam.
No. 1 ..	6,000 BBLS.P.D.	760° F.	3000 LB/HR at 600° F.
No. 2 ..	6,000 BBLS.P.D.	825° F.	3000 LB/HR at 600° F.
No. 3 ..	9,500 BBLS.P.D.	550° F.	2000 LB/HR at 550° F.
No. 4 ..	10,000 BBLS.P.D.	550° F.	2000 LB/HR at 550° F.



No. 1.	No. 2	No. 3.	No 4.
Gasoline. Gravity, 58·5° A.P.I. 90%, 392° F. E.P., 420° F.	Gasoline. Gravity, 58·5° A.P.I. 90%, 392° F. E.P., 420° F.	Gasoline. Gravity, 62·0° A.P.I. 90%, 336° F. E.P., 350° F.	Gasoline. Gravity, 59·0° A.P.I. 90%, 390° F. E.P., 426° F.
Kerosine. Gravity, 41·0° A.P.I. I.B.P., 425° F. E.P., 490° F.	Kerosine. Gravity, 41·0° A.P.I. I.B.P., 425° F. E.P., 490° F.	Naphtha. Gravity, 44·5° A.P.I. I.B.P., 368° F. 50%, 404° F. E.P., 441° F.	Kerosine. Gravity, 40·4° A.P.I. I.B.P., 428° F. E.P., 540° F. Flash, 205° F.
Gas Oil. Gravity, 36·5° A.P.I. I.B.P., 480° F.	Gas Oil. Gravity, 36·5° A.P.I. I.B.P., 480° F.	Cracking Stock. Gravity, 37·3° A.P.I. I.B.P., 540° F. Flash, 300° F.	Gas Oil. Gravity, 35·8° A.P.I. I.B.P. 552° F. Flash, 310° F.
Wax Distillate, 18-20%. Gravity, 30·5° A.P.I. 75-80 viscosity at 100° F. Cold test, 75° F. Flash, 280° F.	Wax Distillate, 18-20%. Gravity, 30·5° A.P.I. 75-80 viscosity at 100° F. Cold test, 75° F. Flash, 280° F.		
Wax Slop, 2%. 70-80 viscosity at 210° F.	Overhead Cylinder Stock, 7-8%. 120-130 viscosity at 210° F. Flash, 520° F.		
Cylinder Stock, 9-10%. Gravity, 20·5° A.P.I. 200 viscosity at 210° F. Flash, 540° F.	Flux, 4-5%. Gravity, 12° A.P.I. Flash, 625° F.	Fuel Oil, 45%. Gravity, 26·8° A.P.I. I.B.P., 562° F. Flash, 340° F.	Fuel Oil, 45%. Gravity, 26·0° A.P.I. I.B.P., 565° F. Flash, 340° F.

FIG. 2.

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In general, tube-still distillation may be classified under two main heads:—

(1) The "once through" or single flash tube still using either a single or multiple fractionating tower system, and (2) The "step up" system involving the use of two or more tube stills and towers operated in series.

In addition there is the circulating type of tube still, but its usefulness for prime distillation is at the moment apparently somewhat limited, although it has a definite field in certain intermediate refinery operations.

The choice between the "single flash" and the "step up" system depends largely on the products to be secured. For ordinary topping or stripping operations the single flash system has distinct advantages, but if desired to cut deeply into the crude for lubricating stocks then the "step up" or "series" system is advantageous, as it lends itself to vacuum operation. By the "step up" system the light products are removed under atmospheric distillation, and the residuum is then treated in a second tube still and tower for the heavier products secured under more or less high vacuum.

Efforts have been made to distill a crude oil by the "once through" method under atmospheric pressure to yield both light and heavy products, and encouraging success has been met in this direction. Such an effort possibly represents one of the most drastic advances in distillation methods that has been commercially adopted, and it may be of interest to examine some of the results obtained before discussing the equipment used. Figure 1 indicates results secured by distilling Pennsylvania crude oil alternatively to cylinder stock and long residuum in the same unit, and the flexibility to vary the products is clearly demonstrated.

Figure 2 shows four different methods of operating a "single flash" unit under atmospheric pressure on Mid-Continent crude oil. This is of interest as indicating the possibility of varying both the light and heavy products.

Distilling Unit.

Let us examine a typical lay-out of a "single flash" tube-still unit to secure results similar to those already discussed.

Figure 3 represents a topping unit to handle a crude oil yielding gasoline, kerosine and gas oil as overhead products together with residuum fuel oil. It will be noted that the crude oil is first used to cool the fuel oil, and is thereby preheated to a temperature of about 300—350° F., after which it passes directly to the tube still, where its temperature is elevated to that necessary to liberate the required amount of overhead product. The crude oil passes directly to the

fractionating tower, which also functions as a vaporiser or separator. It should be noted that the "single flash" method takes full advantage of the partial pressure effect of the light vapours. The practical value of the light vapours has been demonstrated by the experiments of Leslie and Good, described in their article, "The Vaporisation of Petroleum" (*Industrial and Engineering Chemistry*, April, 1927).

Leslie and Good show that a certain crude oil if heated to 600° F., and then vaporised, will yield 78 per cent. of distillate. The same crude oil, if vaporised by successive flash resulting from the formation of equilibrium between vapour and liquid at several temperatures, is only 59 per cent. at the same final temperature of 600° F. The importance of this fact is particularly evident when cutting deeply into the crude oil involving final temperatures of 750° F. to 850° F.

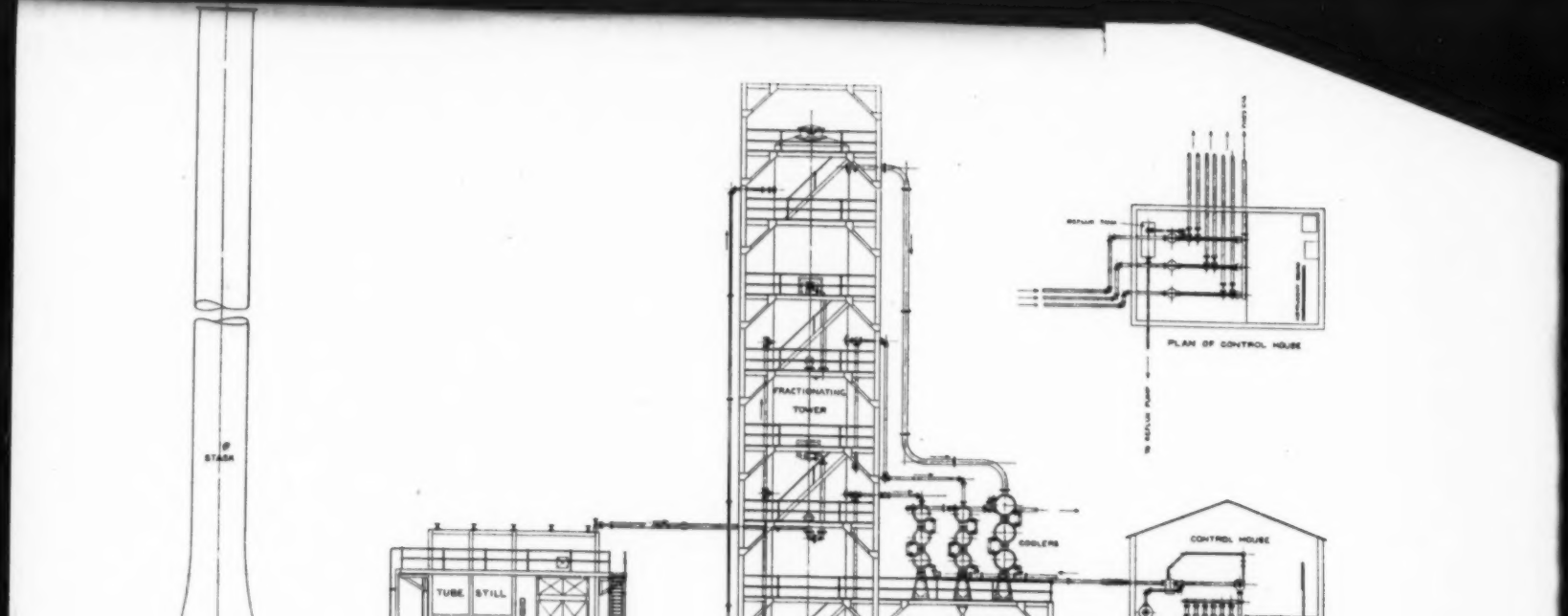
Furthermore, Leslie and Good show the total heat required, for the same per cent. vaporised is less by the "single flash" than by the "step up" or successive flash.

The vaporising portion of the fractionating tower separates the total oil into the liquid residue and a homogeneous vapour comprising all the overhead distillate products. The liquid residue or fuel oil passes through the heat exchangers and is cooled to a temperature at which it can be handled. The vapour passes up the tower and is divided or fractioned into the various products. The lighter ends are obviously at a temperature much above their boiling-point, and to secure these products in the form of liquid streams involves the removal of a certain amount of heat, and this is accomplished by the use of either a partial condenser located above the tower or by liquid reflux pumped back into the tower.

We see, therefore, that heat has first to be transferred into the oil and later removed from the oil, and perhaps the value of a distilling unit can be measured by the efficiency with which these two operations are carried out. Part of the necessary heat is introduced into the crude oil by utilising it as a cooling medium, the remainder being supplied by the burning of fuel in the combustion chamber of the tube still.

Tube Still.

Oil is not a good conductor of heat, and if overheated will break up into carbon and undesirable fixed gases at the expense of more valuable products; and it is important, therefore, to control the rate at which the surface absorbs heat from the furnace. Heat is absorbed in two different ways: by radiation from the furnace or heated brickwork, and by convection while in contact with the hot gases produced by combustion. One of the most important


STACK
TUBE STILL
FRACTIONATING TOWER
COOLERS
CONTROL HOUSE
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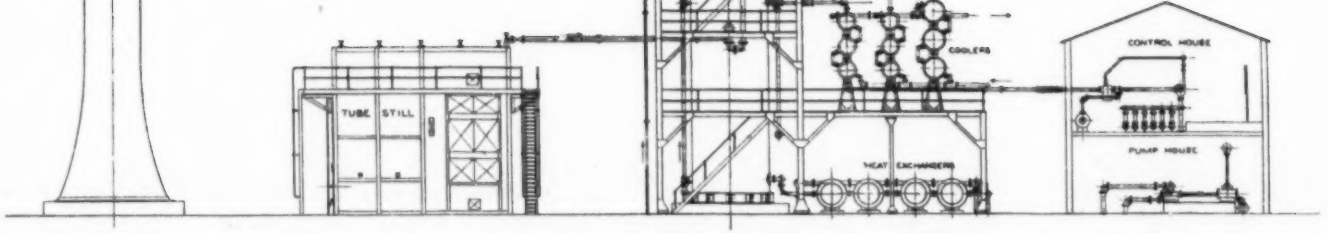
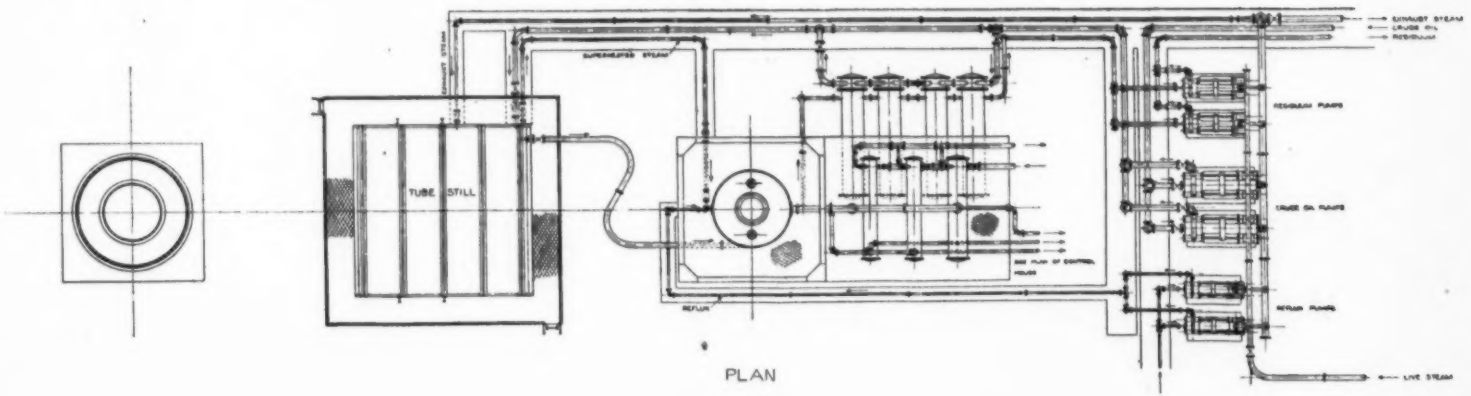


SIDE ELEVATION



PLAN

FIG. 3.

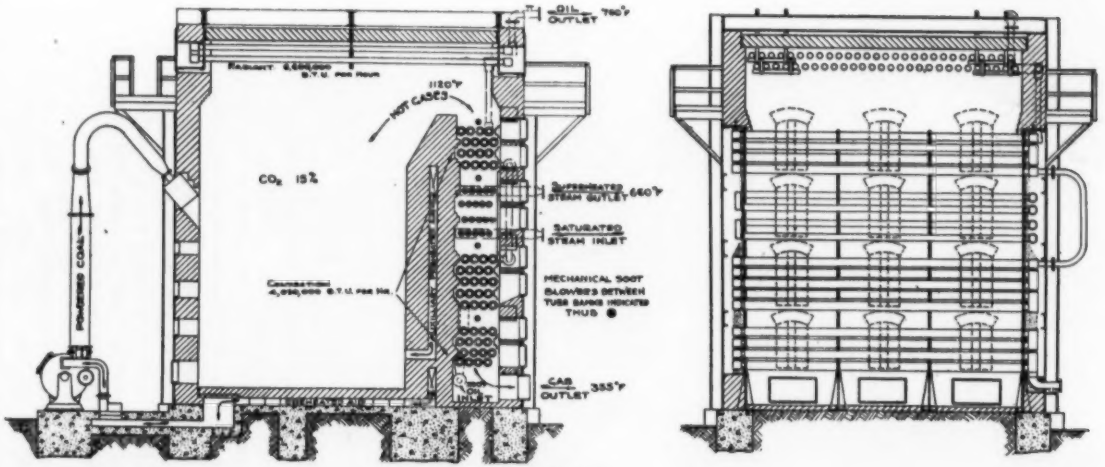


FIG. 4.

SECTIONS THROUGH TUBE-STILL, SHOWING ARRANGEMENT OF RADIANT AND CONVECTION HEATING SURFACES AND POWDERED COAL BURNING EQUIPMENT.

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Improvements in the design of tube stills has resulted from a fuller appreciation of the importance of radiant heat and the more complete proportioning of the radiant and convection heating surface. If heat is supplied to the surface at a rate beyond the capability of the oil to absorb it there is danger of overheating both the tubes and the oil, so that in the earlier type of tube still the fuel was burnt with considerable quantities of excess air. The thermal efficiency could only be improved by burning the fuel with less excess air resulting in a higher furnace temperature, and in some cases this was controlled by returning a portion of the flue gas to the furnace.

It has been found however, that if the absorbing surface is so located and proportioned that sufficient heat is absorbed by radiation, it is possible to prevent excessive furnace temperatures. Additional radiant surface has permitted the fuel to be burnt more efficiently, and at the same time the furnace temperature adjacent to the absorbing surface has been materially reduced.

A. G. Peterkin, junr., discussing "Tube-Still Distillation (Eighth Annual Meeting American Petroleum Institute), has shown that when operating at a thermal efficiency of about 75 per cent. measured by comparing the input of heat into the oil with the heat liberated from the fuel burned, that the furnace temperatures adjacent to the radiant surface varied from 1630° F. to 1360° F. with a final oil temperature of 797° F. The temperature of the oil entering the tube still was 349° F., and the flue gases entering the stack were 490° F. The radiant surface comprised some 16 per cent. of the total surface and absorbed about 53 per cent. of the total heat.

A tube still equipped to burn either powdered coal or fuel oil and having a large furnace volume has been operated for many months at relatively high thermal efficiencies with complete success.

TUBE-STILL PERFORMANCE ON PENNSYLVANIA CRUDE.

Fuel burned.	Coal.	Fuel Oil
B.Th.U. value of fuel	12,800/lb.	136,000/gal.
Thruput—42 gallon barrels per day	1,900	1,830
Temperature of oil entering still—°F.	290	270
Temperature of oil leaving tube still—°F.	760	770
Vaporisation—% of thruput as shown by bottoms plus excess vaporisation	90·0	90·0
Temp. of gases entering convection surface—°F ..	1,120	1,010
Temperature of gases leaving convection surface—°F	355	385
Temperature of steam leaving superheater—°F ..	660	670
Pressure of steam entering superheater (moisture 2%)	26	24
Weight of steam used per hr.	1,390	1,600
CO_2 in furnace—%	15·0	13·0
CO_2 in flue—%	14·3	11·5

Fuel consumption—pounds or gallons per hour ..	980 lbs.	100 gal.
Estimated B.Th.U. per hr. absorbed in convection surface	3,740,000	3,580,000
Estimated B.Th.U. per hr. absorbed in steam ..	290,000	365,000
Estimated B.Th.U. per hr. absorbed in convection bank (total)	4,030,000	3,945,000
Estimated B.Th.U. per hr. absorbed in radiant surface	6,600,000	6,780,000
Estimated B.Th.U. per hr. absorbed in unit (total)..	10,630,000	10,725,000
Estimated Thermal efficiency—%	84·8	79·0
Transfer—B.Th.U. per hr. per sq. ft. inside surface to oil in convection section	4,250	4,070
Transfer—B.Th.U. per hr. per sq. ft. inside surface to oil in radiant section	6,680	6,870
Total inside surface in convection section	880 sq. ft.	
Total inside surface in radiant section	987 sq. ft.	

Fractionating Tower.

The application of the tube still to refinery distillation necessitated the development of a fractionating tower that would continuously separate the homogeneous mass of vapour into the products required. Furthermore, such a tower should be flexible, easy of control, and particularly capable of yielding specification products to obviate redistillation, which involves loss of material, increased capital expenditure and manufacturing costs.

Many types of fractionating equipment have been utilised, but there is a distinct trend towards the bubble tray tower as being more positive in action.

For any one method of operation there is a definite heat input into the tower, but as a portion of the vapour must be condensed and partially cooled to effect separation means are provided to remove this surplus heat. Partial condensers installed on the tower top have certain disadvantages, and more definite control is generally secured by pumping back liquid reflux to the top tray.

Crude oil is a mixture of a large number of constituents, and commercial refinery practice does not necessitate separation into pure products; the boiling range, specific gravity, flash-point and viscosity being the principal physical characteristics necessitating control.

The liquid reflux generally adopted for the main control is the lightest cut yielded by the crude oil, and by discharging this on to the top bubble tray it absorbs heat from the vapour with which it comes into contact, resulting in the re-vaporising of the reflux and the condensation of a heavier vapour. The interchange of heat between the vapour ascending the tower and the liquid oil flowing down the tower is aided by bubbling the vapour through the oil on successive trays. There is a temperature gradient throughout the tower resulting from the introduction of cooling

medium in the form of reflux flowing over the bubble trays, which may be regarded as cooling surface, bringing the hot and cold materials into intimate contact.

A single fractionating tower to yield a number of products is in effect a series of towers superimposed on each other, and in addition to the reflux introduced at the top tray it is necessary to provide additional reflux at each point where a liquid fraction is removed. To regulate the characteristics of the various fractions in commercial operation there are provided "reboiling" or "stripping" sections, and these may be incorporated in the tower itself and such stripping sections may be fitted with superheated steam coils to give the required initial boiling-point or flash-point. Reference has already been made to the ability to vary the fractions, but sharpness of fractionation, particularly on the lighter products, is readily obtainable.

Heat Recovery.

It has often been suggested that the ideal distilling unit would be almost self-supporting in so far as direct fuel is concerned. Disregarding fixed charges, fuel may easily be the most expensive refinery item, and any economy in this direction is pleasantly reflected in the annual balance-sheet. The use of heat exchangers for cooling either the overhead distillate products or the fuel oil residue by means of the crude oil to be distilled may result in the latter absorbing a substantial part of the total heat required. The limiting point for heat recovery is the temperature differential between the cooling medium and the products being cooled, and there obviously is a point where this does not justify the additional surface necessary, but in actual practice it is not unusual to find that about 40 per cent. of the total heat liberated may be recovered.

Conclusion.

To the technologist the distillation of crude oil is a fascinating subject presenting endless possibilities for discussion, research and vision. To the refiner it is a commercial problem necessitating the greatest economy in handling a barrel of crude oil in order that the products may be marketed at a profit. Looking back ten years is helpful in realising the improvements in the art—perhaps the inability to look ahead ten years is an advantage.

It is hoped that it has been demonstrated that tube-still distillation is a distinct advance on the relatively older types of equipment, and the continued application of scientific facts, refinery experience and commonsense will result in still further development.

DISCUSSION.

The Chairman said there was one point of historical interest which, before throwing open the paper for discussion, it might be worth while to mention. In many ways the coal tar industry had led the way in developing the technique of petroleum refining. He remembered some twenty or more years ago going to the South Metropolitan Gasworks in East Greenwich and seeing what he thought must be the original pipe still; that was invented by Lennard in the '70's. That little pipe still was made of ordinary 4-inch cast iron pipe and handled, if he remembered rightly, some six million gallons of coal tar a year. It had no bubble tower equipment; it merely passed the vapours into a series of fractional condensers, producing the chief technical fraction of coal tar. He imagined—the author might be able to confirm it—that the pipe still became practical politics with the development of cracking. Until the big modern cracking units had definitely shown the advantages of the pipe still, little was done in the industry to apply facts which were already well known.

Mr. N. A. Anfilogoff said the Chairman—quite unwittingly, no doubt—had already referred to much that he himself had intended to say, and he stated, quite rightly, that the modern tube-still was an emanation of very ancient gasworks practice, not necessarily for distilling. He did not know until the Chairman mentioned it that it was being used by the gas industry for distillation, but for almost as long as coal tar was known in the gas industry a pipe-still or tube-still was utilised for dehydrating tars. The tars contained a considerable amount of water. It was necessary to get rid of the water, and it was found that the only way to get rid of the water safely and quickly was to put the wet tar through a coil which was heated in a furnace, and the water was separated out as steam in a separating tank.

He did not altogether agree with the Chairman that the tube-still had come into its own only since cracking came before the eye of the technologist. It must be remembered that the tube-still had been at work very efficiently for quite a number of years now. If the author would permit him to say so, the title of the paper was not altogether accurate. Nothing new in the way of tube-stills was dealt with in it—nothing that had not already been seen or known from other illustrations,—but the author had given many very interesting details about the bubble tower.

He wished to say a word or two about the bubble tower. Bubble towers had no doubt been developed considerably, and there were now bubble towers 15 feet in diameter and 100 feet high. It would have frightened the engineer of yesterday to contemplate an erection

like that and—since probably he belonged to yesterday—it certainly frightened him to think of an erection 100 feet high, with numbers of decks, as the Americans called them, or floors, as they were known in this country, all the way up. He could not help wondering what would happen to such a beautifully erected steel structure if something happened on the ground floor and a pipe broke, a flange gave out, or for some other reason there was a fire.

As a practical refiner he thought the striving after thermal efficiencies could lead to an *impasse* and lead to a considerable capital outlay without any corresponding benefit. The method for calculating the thermal efficiency used in the paper appeared to depend on a series of assumptions—or, as the author called them, estimates—which rendered the checking of the results very difficult indeed. If one took a fuel consumption of 100 gallons an hour, that gave rise to 13,600,000 B.Th.U.'s per hour. The author then stated that 3,945,000 B.Th.U.'s were absorbed per hour in total convection and 6,780,000 B.Th.U.'s per hour in total radiation, giving a total B.Th.U. value absorbed of 10,725,000. No data were given to indicate how those figures were arrived at. The efficiency, which the author gave as 79 per cent. for his plant, was obtained as the ratio of the total estimated B.Th.U.'s absorbed to the B.Th.U. value of the fuel combustion.

He had had a tube-still working for a number of years. So far as the bubble tower was concerned, the Chairman would remember a Heckmann type bubble tower erected at Thameshaven, where an attempt was made to distil pure toluol from cracked petroleum distillate. So far as the tube-still was concerned, and especially in connection with the fractional condenser, he was afraid not sufficient was made of it ; he did not think very many refiners had had the courage of their convictions and had really tried out fractional condensing for the purposes of fractionation.

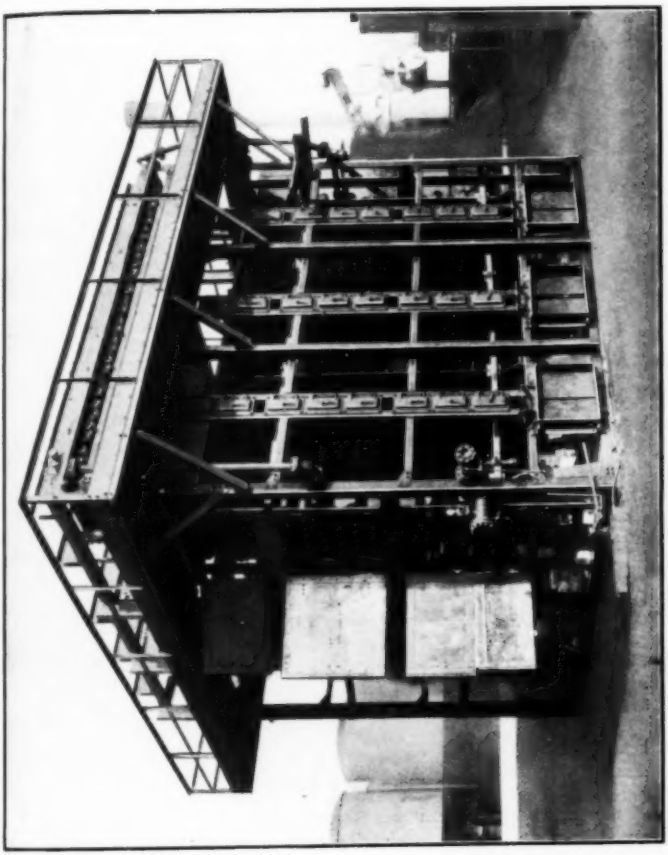
He had calculated the efficiencies of a certain tube-still he was working on, and going by the figures the author gave and working out the over-all efficiency of the tube-still (the author's figure of 79 per cent. was for thermal efficiency only), he found that his own tube-still worked out at something like 17 per cent. more over-all efficiency than the author's. Working out the author's figures by the method he (the speaker) had adopted, the over-all efficiency of the tube-still for which the author gave figures came out as 30 per cent., whereas in the case of the one at Thameshaven the figure worked out at 47·77 per cent. In the case of the particular still for which the author worked out the figures, there was a throughput per hour of 13·33 tons or thereabouts. Fuel consumption apparently was 3·3 per cent. of the crude put through. It was true that in that particular distillation a 27 per cent. residue was

being worked to. Working on a Venezuelan crude at Thameshaven with 51 per cent. of distillates taken off, and running on a throughput of 56·54 tons per hour, the fuel consumption was 0·627 tons, which worked out at 1·1 per cent.

He thought the author was perfectly right in the concluding remarks of his Paper, namely, that however interesting the matter might be to the technologist, when the technologist had to apply his knowledge to earning profits, £ s. d. came into it. It was curious to note that on one occasion when he attempted to try it out, a loss of 9 per cent. in actual over-all efficiency but an increase in throughput resulted in making £200 per day extra profit. That went to show that the striving after absolute thermal efficiencies and absolute efficiencies did not necessarily lead to one's getting results. As an example, one might take the case of a steam-pipe which was lagged. The usual practice was to have about 2 inches of lagging, and no one would suggest that in that case one was losing no calories at all; but if one put another half or even quarter-inch of lagging to try to retain the few calories that were lost, it would be found that the capital outlay was not worth it and one would gain nothing in actual efficiency.

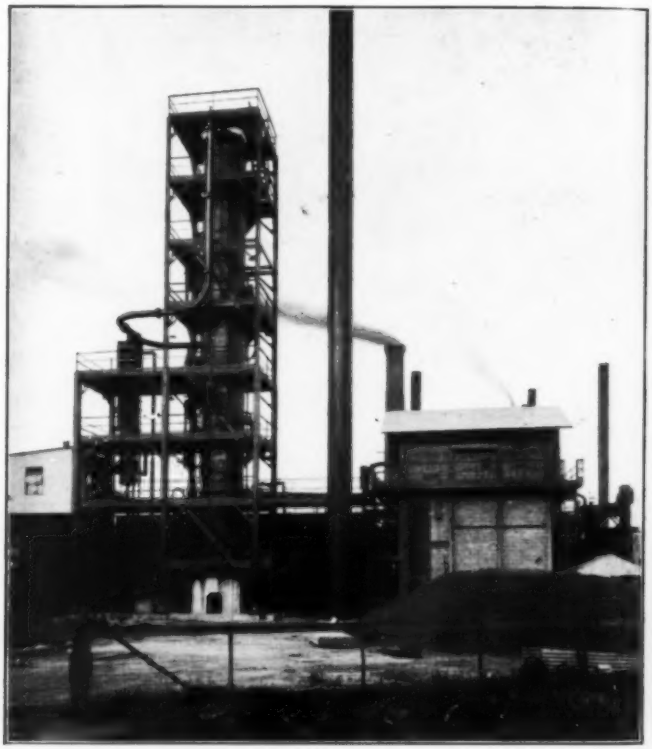
It would be remembered that in the case of tube-still distillation there were two peculiar phenomena to consider. The first was the stream-line flow of a fluid going through pipes.

If the pressure was increased there was an increase in the velocity up to a certain point, but up to a certain point only; beyond that point there was no increase in the velocity of any value. That, however, was another question. A considerable further increase of pressure brought one to a second point, which was reached when the further increase of pressure gave an incremental rise in the velocity. That was the second phenomenon, and was called turbulence. In all tube-stills it was due to that turbulence that the liquid, instead of going in concentric cylinders, was rolling and eddying through the pipe. It was that which enabled the heat which was absorbed from the walls of the tube to be conveyed to the core. The turbulence factors were very well known, but it must be remembered that when or if that turbulence was allowed to become too turbulent one was bound to get, instead of a rolling and eddying movement, actual hot spots which were covered by no oil at all; with the wave action of the oil through the tube one would get uncovered tubes and a chance of local overheating. The tube-still had therefore to be designed with due regard to that. He was sure that with any tube-still which depended chiefly on the absorption of radiant heat alone, however much one might protect the outside, if the pressure got beyond the critical stage and the

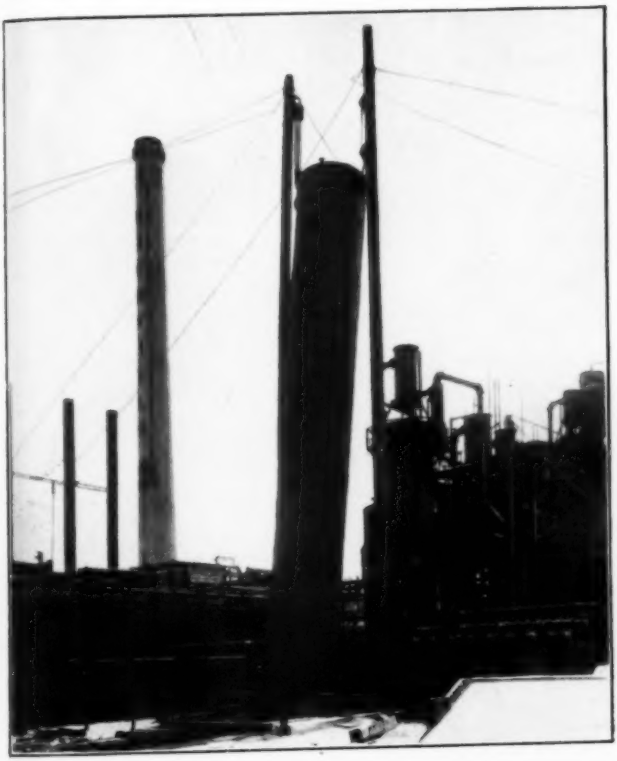


TUBE STILL ERECTED READY FOR BRICKWORK SETTING.

UNIV. OF MICH.

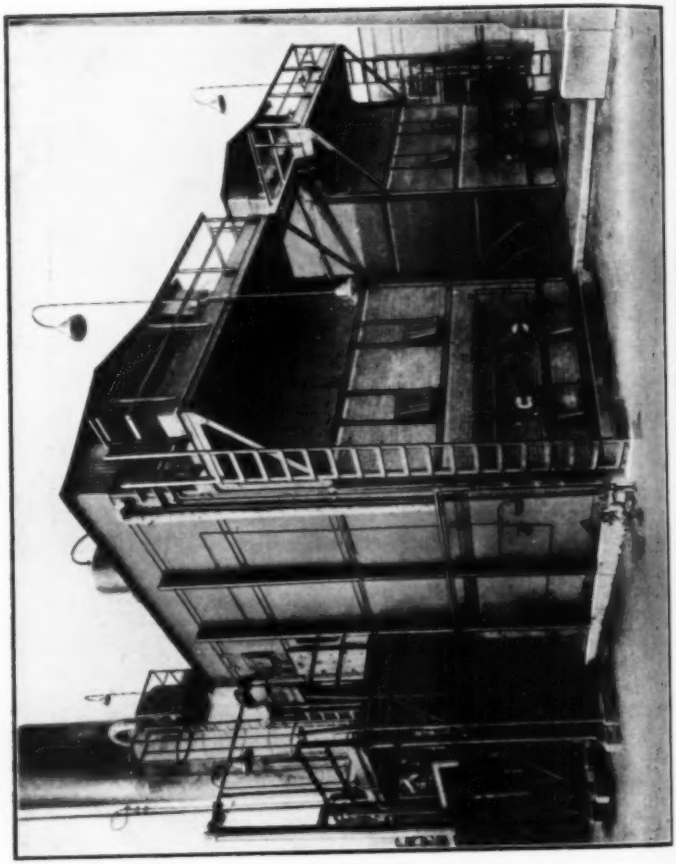


DISTILLING UNIT OF THE SINGLE TUBE STILL AND FRACTIONATING TOWER TYPE.



ERECTING A LARGE FRACTIONATING TOWER.

UNIV. OF MICH.



turbulence became more than an eddy one would be bound to get the tubes burning out.

He did not say the tube-still to which he was referring had been designed with any particular excellence ; it might be that he had been fortunate. He was not referring to a tube-still which had been in operation for two months, but was speaking of a period of at least two years, during which two pipe-stills—he called them retorts—were working together at the rate of 1,500 tons a day and had, during the past two years, put through just over 800,000 tons of crude oil. The total amount of expenditure on repairs and maintenance during that period was nil, putting on one side a sum of £7 which was spent to take the flanges off for a general inspection. That was the sort of thing one had to look for and the sort of thing which would be obtained if the tube-still were properly designed and worked ; but one must not run away with the idea that the tube-still could do everything that was done by the shell-still. With the best bubble tower in the world, even if the author were to raise it another 100 ft. and make it 20 ft. in diameter, one could not get from a bubble still a special boiling-point. One could take off a small amount, but it would certainly never pay a refiner who was processing at the rate of 3,000 tons a day in two of these bubble towers to take off small fractions. For that purpose one was bound to have the steam still, which was necessary for the distillation of some of the special boiling-point oils. Not only that, but in this country at any rate people were more fastidious and required a very much clearer cut distillate and end-points than those permissible in the United States, where the 220° C. end-point was the rule rather than the exception. One could take that off, no doubt, quite easily.

He wished to say one word more with regard to condensers. On the particular tube-still to which he referred there were five fractional condensers. Fifty-one per cent. of the products was taken off, and the first one gave the gas oil fraction ; the second one gave the heavy kerosine ; the third a white oil with a final evaporating point of about 230, while the product of the next two was spirit and could be split into two or—as in fact was done—mixed. He wished to point out that with fractional condensing alone one was able to get, if the process was properly worked, a variation of 5° C. between the final boiling-point of the one and the initial boiling-point of the other product, and he would sooner have that at a height of 30 ft. than a bubble tower at a height of 150 ft.

Mr. A. A. Ashworth said it was stated in the paper that if crude oil was heated to a temperature of 600°F. in a tube-still and then vaporised, there would be a certain percentage result. That rather lent colour to an idea which had been voiced before,

that in a tube-still the oil was merely heated up to a certain temperature, and that vaporisation did not take place until the oil was delivered into the vaporising space of the tower. That had been stated once or twice, but he thought it must be a mistaken view.

Most vaporisation must take place in the actual tube-still; there was evidence of that in the high pressures necessary to force the crude oil through the considerable length of piping into the tube-still. The pressures were so high that the extra friction of the vapours developed in the pipes caused pressures of 75, 80 and even 100 lbs. to be employed. If the oil were to be heated up without vaporisation in the pipes at all, it entailed a considerable amount of superheat in the oil, which would be against good distillation and would induce cracking.

He wished to point out that, although Messrs. Leslie and Good had called attention to the increased percentage of distillate obtained by a single flash distillation in a tube-still compared to the percentage obtained in a boiler-still or by successive flash distillation in a tube-still at the same temperature, the matter had been previously brought forward in a paper by himself. (A Pipe-Still for Continuous Distillation in the Laboratory, and some Results obtained from it. Journ. Inst. Petr. Techn., 1927, XIII. (60), 91-100).

He wished to ask whether steam was used in the still itself; he noticed one of the illustrations showed a connection going into the tube-still. Free steam was, of course, used in the stripping sections.

With regard to a single bubble tower, if one had a large number of cuts to make it meant that one must restrict the number of trays or plates to each one cut, or get a bubble tower which would be altogether out of reason in height. In some cases for each cut as many as 12 plates were used; he thought in the author's tower there were 6. He presumed that gave sufficient separation.

Then there was the question of regulation. He thought it possible that in a single tower the additional refluxes might alter the equilibrium all the way down the tower.

There was one point which the author had not mentioned with regard to the benefit of tube-still distillation and bubble towers. This was the question of the value of the yields obtained from the crude oil. He had recently had occasion to test one of the usual type of continuous boiler-still installations and to compare the actual returns of the standard product obtained from the refinery with the returns shown to be obtainable in the laboratory of the same standard product from the same crude oil. He found that the value of the refinery returns was only some 85 per cent. to 87 per cent. of what could be obtained from the crude oil. With

a tube-still and bubble tower equipment, and especially with one making actual gaps between the cuts as the author had shown, it would be possible to obtain practically 100 per cent. efficiency of value and the difference between these results far outweighed any benefit from the saving of fuel and rerunning.

Mr. N. A. Anfilogoff asked if from his experience in the United States the author could give some slight indication of what a complete unit dealing with 1,500 tons a day, to take off, say, 50 per cent. distillate, would cost, and what it would cost per ton to operate.

Mr. C. H. S. Edmonds, in reply, said it had been interesting to hear Dr. Dunstan refer to the coal tar industry. In the development of the first few tube-stills for handling coal tar there was only Lennard's previous experience available, and due credit should be given to the coal tar industry for its pioneer work in this direction.

Originally, tube-stills were used principally for removing only the light ends—20 per cent. or 25 per cent. of gasoline. Then came the development of cracking, and it was found that the tube-still was capable of doing a great deal more real work ; but during that time the coal tar industry had been quietly operating tube-stills to temperatures as high as those reached in a modern cracking unit to-day. In passing, he might mention that tube-stills for coal tar were originally built entirely of cast iron. Neither forged steel nor cast steel was used.

Many people disliked the idea of a bubble tower 100 or 120 feet high, but that evening he was submitting results which had been secured from equipment built in that way. It was often said the United States liked to do big things in a big way, and consequently if instead of using 3 bubble towers they could put them on top of each other and have one, they perhaps felt happier about it.

Perhaps he might tell Mr Anfilogoff that the steel structure round the tower was in no way used to support the tower itself, but only to provide means of access to the tower. Towers of that size were entirely self-supporting ; the whole steel structure could come down and the tower would still remain standing,

It was perhaps a little dangerous to quote thermal efficiencies, but Mr. Anfilogoff would at least admit that the word " estimated " appeared in the paper in front of the words " Thermal efficiency." (*Mr. Anfilogoff : Yes.*) He was not trying to maintain there that a tube-still or even a distilling unit should be operated at the greatest possible thermal efficiency. It was, however, of interest to realise that tube-stills had been operated to give relatively high thermal efficiencies compared to those with which one was accustomed to meet in the refining industry. It was always difficult to form

a basis of comparison. He frankly admitted he ought to have said that the results he quoted were based on a certain specific heat and latent heat, both of which had to be assumed for the purpose of giving the efficiencies. Furthermore, the particular results which perhaps seemed high—although he did not think Mr. Anfilogoff considered they were anything out of the way—were largely obtained under test conditions. There was, however, no question whatever but that tube-stills could be operated and were being operated at a thermal efficiency within the tube-still itself of 70 to 75 per cent. as a commercial every-day operation.

He hoped Mr. Ashworth would accept his apology for referring to Leslie and Good when he could easily have referred to Mr. Ashworth's own paper, which he had read very carefully; in fact, he had had the pleasure of discussing it with Mr. Ashworth. He did not think it could be questioned that there was a considerable amount of vaporisation taking place within the tubes of the tube-still and the pressure loss was, of course, much higher when handling a mixed vapour and liquid. A point was raised about the pressure of the oil producing a certain type of flow. He thought the pressure in the last part of a tube-still could be practically nil—say 5 or 10 lbs. On the other hand, fairly high pressures were encountered at the charging pump when operating on the once-through system, because there was the pressure loss in the heat exchangers and the pressure loss in the tube-still to be taken into account, and it was not unusual for that to amount to anything from 100 lbs. up to as high as 300 lbs. pressure, necessitating the equipment being built to withstand that.

As a general rule it was not customary to put steam into the tube-still itself; there was a connection whereby steam could be put through a separate superheater incorporated in the tube-still setting to secure superheated steam to operate the stripping sections of the tower. Previous mixing of steam with the oil had been tried, but not generally adopted.

With regard to the control of the fractionating tower, there was a main control generally comprising an automatic temperature control fitted on the vapour outlet of the tower. The ratio refluxes or sub-refluxes then had to be adjusted to give the required characteristics, and obviously if one changed the characteristics of one fraction one must of necessity change the characteristics of at least one more, either the one immediately lighter or the one immediately heavier. In actual operation the single tower with its ratio reflux was probably no more difficult to control than a series of towers which necessitated the pumping back of the reflux to each one of those towers. He thought it did not make much difference whether it was regarded as a single tower or as a series

of towers; it was necessary to put the reflux into each one of them, necessitating a control operation.

So far as cost was concerned, that was always a dangerous ground on which to venture, but he thought that generally speaking it had been shown that a tube-still unit could be built for less than a shell-still unit giving equal final results. In general he thought it would be found that in the United States the tube-still unit cost probably about 70 per cent. of the cost of the shell-still unit. The operating cost depended so much on local conditions that it was almost impossible to give it, but in general the tube-still unit had shown itself susceptible to less operating labour than the shell-still unit. It was difficult, however, to get a very good comparison between the two units, because one did not as a rule find the two units—a shell-still unit and a tube-still unit of the same capacity and doing the same work—in the same plant, and therefore comparisons were very difficult.

In conclusion, he wished to thank the members of the Institution for the way in which they had received the paper, and for the kind and helpful criticisms which had been made.

On the motion of the Chairman, a very hearty vote of thanks was accorded to Mr. Edmonds for his paper, and the proceedings then terminated.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND TWELFTH GENERAL MEETING of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, W.C. 2, on Tuesday, May 8th, 1928, Sir Frederick W. Black, K.C.B., Past-president, in the Chair.

The Secretary announced that applications for grants from the Research Fund should be in his hands by June 1st next; that a meeting of the Students' Section would be held at 5.45 p.m. on Tuesday, May 22nd, at Aldine House; and that the Annual Dinner would be held at the Connaught Rooms on October 3rd next.

The following gentlemen had been elected members of the Institution :—

Member.—Mircea I. Oreviceanu.

Associate Members.—Christiaan Antoon Bauduin, Arthur Ellis Owen Cooke, John Cecil Jones, Thomas William Robinson.

Students.—Heath Roydon Hose, Edward Ainslie Penson.

Associates.—Archibald Thomas Bacon, William Henry Taylor.

The Chairman said that the present meeting was the last of the session, and that the next meeting would take place on October 9th next. He was sorry to find himself in the Chair again that evening, but the President and other members were attending the dinner of the Institution of Mining and Metallurgy. The subject dealt with by the Paper about to be read was "Experiments in Viscometry." He had an open mind on the subject in regard to light products, because all he knew about viscosity was in connexion with heavy fuel oils. There were several gentlemen present who were experts in the particular branch of the subject to be dealt with that evening, and he hoped they would join freely in the discussion which would follow the reading of the Paper.

The following Paper was then read :—

Experiments in Viscometry.

BY H. S. ROWELL, O.B.E., F.Inst.P., M.I.Mech.E., M.I.A.E., AND D. FINLAYSON, M.C., M.A., B.Sc., A.I.A.E.

INTRODUCTION.

The following Paper is based on reports that have been issued during the past five years to Members of two Research Associations. Actual needs of practice led to the inception of the work and

governed the methods and sequence adopted. It is hoped, therefore, that the results may be of interest and value to Petroleum Technologists. If some of the conclusions submitted are not highly novel, as least they are to be regarded from one point of view, that of the user, and this is a considerable advantage. Oil and fuel interests are now so diverse and widely spread, units and testing methods are so multifarious, and the attitudes of the oil refiner and user are so different, that information, when available and reliable, is not always readily applicable.

In the study of carburation, which is essentially the precise measurement of minute quantities of volatile fuel induced to flow by a stream of air, viscosity and density as dependent on temperature are obviously of the first importance. From the results obtained in this work it appears possible that viscometry combined with densimetry may be an effective instrument in the analysis or identification of complex carburants.

Lubrication, as is well known and now obvious, is greatly dependent on the viscosity of the lubricant. And since in much modern machinery, conspicuously the millions of automobiles in daily use all over the world, lubrication of hot surfaces is necessary, it is important to know how the viscosities of lubricants vary with temperature. When this work began, very little reliable information was available on the viscosity of oils at temperatures much above 100° C., and, perhaps, more regrettable, no sure method of extrapolating existing information to high temperatures could be found. Efforts were therefore made to obtain data on these two points. In the course of the work it became apparent that the usual viscosity curve is geometrically very ill-conditioned, and therefore an attempt was made to devise a suitable characteristic curve for lubricants; this is offered more as a preliminary suggestion for discussion than as a completed recommendation.

Before proceeding to the experimental results it is perhaps desirable to review very briefly some recent tendencies in regard to lubrication theory. For some years now it has been realised that solid surfaces exert a marked influence on liquids in contact with them. In some branches of science this influence has been ascribed to the "adsorption" of the liquid at the solid face; in recent investigations in lubrication, notably by Sir W. B. Hardy, F.R.S., this liquid-solid action has been adduced to explain a phenomenon now comprised under the term "boundary lubrication."

A simple analogy may help to illustrate these points. Consider a flat bottomed punt floating in shallow water. Beneath the water are flat rocks covered with weeds and slime. As the punt is more heavily loaded it sinks, and the layer of water beneath it becomes thinner—as the oil film in a bearing becomes thinner

under load. So long as the punt is afloat it moves freely, but if under heavier load it comes in contact with the slime and weeds, the motion is much more difficult though smooth. If now the punt is still further loaded, the slime and weeds are crushed and torn from the rocky surfaces and the punt is abraded at the points where it touches the rocks. If the punt and the rocky bottom were assumed magnetic, the analogy might be more complete but it would be less simple.

In this picture the water is the lubricant film, the weeds and slime are the boundary layer of adsorbed molecules and the abrasion at the points of contact is equivalent to the scoring and seizing that occurs when lubrication is faulty. In some quarters a good deal of undue importance has been attached to this ultimate phase in the lubrication problem, with the result that viscosity, which is the predominant physical property of a lubricant and the inhibitor of the boundary condition, has, by some, been given second place. The fact, well known for many years to the older millwrights and engineers, that castor oil and tallow ameliorate the tendency to seize and run hot in many bearings is in good agreement with recent work on boundary lubrication. But neither the experience of the millwright nor the experiments of Sir William Hardy justify the use of the popular word "oiliness" to express the superiority of the animal and vegetable oils in extreme conditions. It is abundantly clear both in millwrighting and in boundary lubrication experiments that the metals at the boundaries play an important part.

Moreover, in recent work a new question of supreme interest has arisen. When bearings are overloaded, local pressures may become very high and the consideration at once arises as to whether oils change in respect of viscosity when under very high pressures, and, if so, whether all oils change equally in this respect. The work of Stanton and Hyde in 1920 answered these questions with apparent conclusiveness. It was shown that a mineral oil under heavy pressure gained proportionately much more viscosity than did a vegetable oil, and therefore the so-called "oiliness" property could not be explained as pressure-conferred viscosity. More recently, however, Hersey in America has carried out experiments under much greater pressures and finds that at these pressures the viscosity relations for mineral and non-mineral oils are not so simple as had been supposed. It is obviously too early to indulge in final deductions, but enough has been said to make abundantly clear the importance of viscosity and to justify careful viscometry. Even if the present knowledge of boundary lubrication should need no reformation, it would not follow that the older views of viscosity are to be entirely discarded. It is a striking fact that

while, on the one hand, Thorpe and Rodger have shown that viscosity increases generally with the molecular weight of the lubricant, Hardy and Doubleday have shown that "boundary" friction co-efficients decrease as the molecular weight increases. If this paradox were general, we should have the simple lemma that viscous lubricants not only inhibit the occurrence of boundary lubrication but they also reduce the friction when the boundary state arrives.

Before concluding this introductory chapter a word on units and notation may be included. In the following pages the C.G.S. unit of viscosity, called, on the suggestion of Deeley and Parr, the poise, after Poiseuille, is taken as the basis. It may be defined as the ratio of shear stress in the liquid to the velocity of shear strain, and so bears a close resemblance to the modulus of rigidity in elasticity. The poise is a very convenient magnitude for the viscosities of oils at ordinary temperatures and its derivative the centipoise, equal to the viscosity of water at 20·2° C., is handy for petrols and for oils at high temperatures. Continental engineers use the kg. metre sec. unit which is 98·1 poises, while the English engineering unit in lb. ft. sec. is 478 poises. The convenience of using one unit needs no emphasis and since the poise is, all round, the most convenient unit, it is to be hoped that it will come into more general use among practical men. Once a viscometer is calibrated, a determination in poises is as simple as in any other units.

In many of the diagrams that follow the ordinates are measured in "fluidity" which is the reciprocal of viscosity. Bingham has suggested the word "rhe" (from the Greek 'rhein—to flow) as a brief and convenient name for the C.G.S. unit of fluidity. Using this word, a liquid of viscosity one poise, would have one rhe of fluidity, and a liquid possessing a viscosity of one centipoise, *e.g.* water at 20·2° C., would have a fluidity of 100 rhes or one centa-rhe. No matter what unit of viscosity be chosen the corresponding unit of fluidity follows simply from it, so that those who prefer to remain loyal to the Redwood second could express fluidity in Redwood "dnoces"—the word "second" written backwards.

The importance of "fluidity" to those concerned with fluids need hardly be indicated. Apart from the fact that fluidity is the primary characteristic of a fluid, various differences among fluids are more conveniently exposed in terms of fluidity than in terms of viscosity or other properties. By the reciprocal definition it follows that fluidity is the velocity of shear strain per unit shear stress, and thus a direct measure of the primary fluid property is expressed. "Viscosity," derived from the Greek for birdlime, or mistletoe, or both, connotes a resistance or negative property

of a fluid, as may be seen in the older and more vulgar meaning of the word—stickiness or glutinosity. Lastly, the more or less accurate additive property of fluidities may be mentioned as an advantage especially useful to those concerned with the precise mixing and blending of liquids.

Viscosity of Motor Fuels.

The property of viscosity is not one which is frequently referred to in relation to the mobile liquids used as fuels for internal combustion engines; yet there are at least three aspects of the problem of carburation in which a knowledge of the viscosity of a motor fuel and its temperature-variation is of interest and importance. The first is concerned with the fact that in a homologous series, with exceptions in some cases among the lower members of the family, the viscosity increases with the molecular weight, and hence the fluidity of a fuel from any one source may serve as an approximate index of its mean or effective volatility. The second is dependent on the possibility that viscosity data combined with density data may afford evidence of the chemical constitution of a fuel. The third relates to the effect of fuel viscosity on the flow through carburettor jets.

In the course of a systematic investigation of the physical properties of motor fuels undertaken by the Research Association of British Motor and Allied Manufacturers in 1923, the viscosities of a number of commercially available fuels were measured over the temperature range 10°—50° C. by means of a Bingham viscometer of the form described later in this paper, the diameter of the capillary being suitably chosen for use with petrols. The results for twelve fuels are tabulated at 10° intervals in Tables II to V, together with measured values of the density and calculated values of the fluidity and kinematic fluidity (fluidity × density). For convenience the fuels are represented by symbols, the key to which is given in Table I. The samples were taken from

Table I.

Fuels tested.

Fuel.	Symbol.
Aviation spirits	A & G
No. 1 spirits	B, F, H & K
No. 3 spirit	C
Vaporising spirit	D
Benzol	L & O
Benzol mixture (50/50)	N
Kerosine	R

TABLE II.

Viscosities of motor fuels—Centipoises.

Fuel.	Temperature, ° C. 10	20	30	40	50
A ..	0·494	0·440	0·395	0·356	0·322
B ..	0·522	0·464	0·415	0·374	0·339
C ..	0·577	0·510	0·456	0·408	0·369
D ..	0·375	0·338	0·306	0·279	0·255
F ..	0·573	0·505	0·452	0·404	0·366
G ..	0·467	0·417	0·375	0·339	0·306
H ..	0·601	0·530	0·472	0·425	0·383
K ..	0·564	0·500	0·447	0·401	0·363
L ..	0·729	0·621	0·542	0·478	0·423
N ..	0·610	0·534	0·474	0·423	0·381
O ..	0·702	0·606	0·530	0·469	0·418
R ..	2·033	1·658	1·383	1·172	1·006

TABLE III.

Densities of motor fuels, 10° C. *to* 50° C.

Fuel.	Densities gms. per c.c. 10° C.	20° C.	30° C.	40° C.	50° C.
A ..	0·726	0·718	0·709	0·700	0·691
B ..	0·736	0·727	0·718	0·709	0·700
C ..	0·740	0·732	0·723	0·714	0·705
D ..	0·691	0·682	0·671	0·662	0·652
F ..	0·740	0·731	0·722	0·714	0·704
G ..	0·730	0·721	0·712	0·702	0·693
H ..	0·759	0·750	0·742	0·734	0·725
K ..	0·742	0·733	0·724	0·715	0·706
L ..	0·884*	0·872	0·862	0·851	0·840
N ..	0·828*	0·817	0·808	0·798	0·787
O ..	0·876*	0·864	0·854	0·844	0·833
R ..	0·814*	0·808	0·801	0·793	0·786

*Values obtained by extrapolation.

TABLE IV.

Fluidities of motor fuels at various temperatures.

Fuel.	Absolute units. Temperature. 10° C.	20° C.	30° C.	40° C.	50° C.
A ..	202·5	227·4	253·3	281·1	310·9
B ..	191·5	215·4	241·1	267·5	295·0
C ..	173·3	196·2	219·4	245·3	271·4
D ..	266·5	295·9	326·8	359·0	392·0
F ..	174·4	197·8	221·4	247·3	273·3
G ..	214·0	239·6	266·9	295·0	326·2
H ..	166·4	188·6	211·7	235·5	260·9
K ..	177·2	199·9	223·8	249·4	275·4
L ..	137·2	161·1	184·6	209·1	236·2
N ..	164·0	187·1	211·0	236·2	262·6
O ..	142·4	164·9	188·6	213·4	239·2
R ..	49·2	60·3	72·3	85·3	99·4

TABLE V.

Kinematic fluidities of motor fuels.

(Absolute fluidity × density.)

Fuel.	Temperature ° C. 10° C.	20° C.	30° C.	40° C.	50° C.
A ..	147	163	180	197	215
B ..	141	157	173	190	206
C ..	128	144	159	175	191
D ..	184	201	219	238	256
F ..	129	145	160	177	192
G ..	156	173	190	207	226
H ..	126	141	157	173	189
K ..	131	147	162	178	194
L ..	121	140	159	178	198
N ..	136	153	170	188	207
O ..	125	142	161	180	199
R ..	40·0	48·7	57·9	67·6	78·1

sealed cans purchased at garages or from drums supplied by manufacturers.

From the tables of fluidity and kinematic fluidity, it will be seen that these properties, particularly the latter, are much more

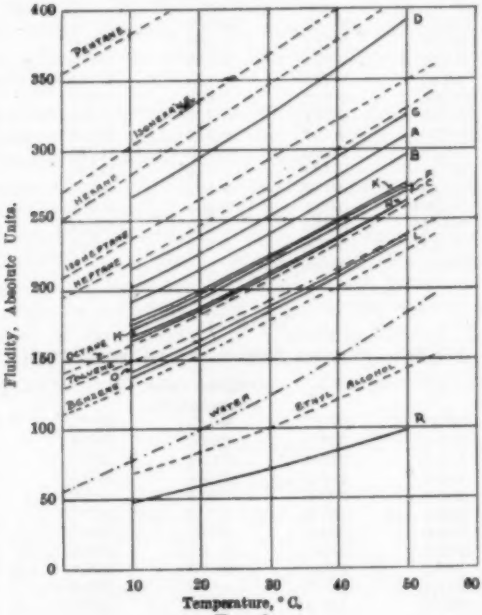


FIG. 1.

FLUIDITY-TEMPERATURE RELATIONS OF MOTOR FUELS.

nearly linear functions of the temperature than is the viscosity. It is convenient therefore, in any work requiring an accurate knowledge of the viscosity of a fuel at an intermediate temperature, to interpolate by means of fluidity curves, subsequently converting to viscosites if required. In Fig. 1 the fluidity results are shown graphically together with published fluidity data for water, ethyl alcohol and representative paraffin and aromatic hydrocarbons. The fact that fluidity serves as at least an approximate indication

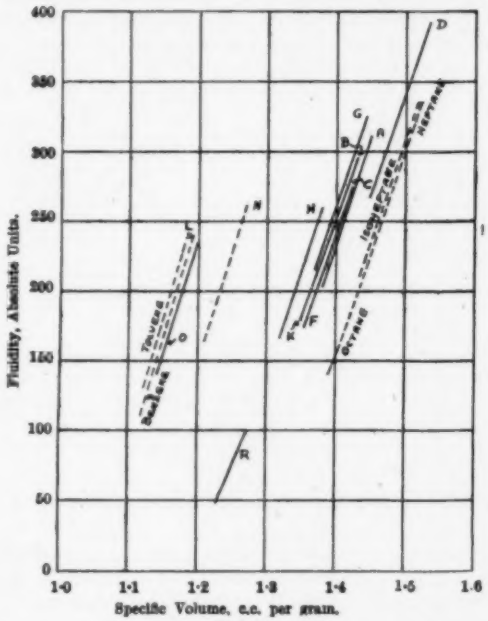


FIG. 2.

FLUIDITY-SPECIFIC VOLUME RELATIONS FOR MOTOR FUELS.

of volatility in chemically related fuels will be clear from these curves. Thus the vaporising spirit has a fluidity intermediate between those of hexane and heptane, while the remaining petrols have fluidities intermediate between heptane and octane, the aviation spirits having values approximating most closely to the former. It should be noted that present-day British petrols are probably appreciably more volatile, and more fluid, than the representative samples purchased in 1923.

The possibility of using viscosity-density data as an index of fuel composition is shown most clearly by plotting fluidity against specific volume at the same temperature as in Fig. 2. With this method of plotting it is usually found that the curves for different members of any one homologous series fall together in a group, in some cases so closely as to form practically a single curve. The significance of this fact is too extensive to discuss at length in the present paper, but it will be clear that if sufficient data were available for each of the different families of hydrocarbons, together with data for representative mixtures, it might be possible to indicate approximately the chemical constitution of a motor fuel from viscosity and density data alone. In Fig. 2 it will be seen that the curves for the two commercial benzols fall in a group with

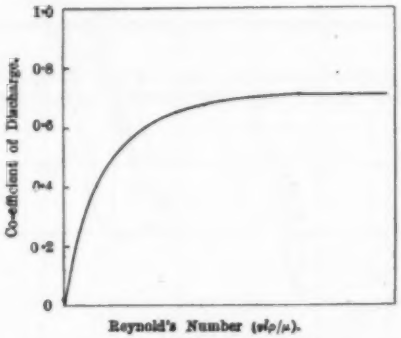


FIG. 3.

VARIATION OF CO-EFFICIENT OF DISCHARGE WITH REYNOLD'S NUMBER ($vl\rho/\mu$).

those for pure benzene and toluene, while the majority of the petrols form a group of curves appreciably displaced in the direction of lower specific volume or higher density from the curves for heptane, octane, etc. Members with special experience will no doubt perceive reasons for this marked displacement and contribute their views in the discussion.

The flow through carburettor jets is affected by the viscosity of the fuel only indirectly, the effect of viscous drag being usually of small importance. The main effect is due to the combined influence of density, jet size, viscosity and fuel speed on the form of the stream lines at the jet, a fact which can be represented mathematically by the expression

$$C = f\left(\frac{vl\rho}{\mu}\right)$$

where C = the coefficient of discharge
v = a characteristic velocity, *e.g.* the mean fuel speed
l = a characteristic linear parameter, *e.g.* jet diameter
ρ = the density
and μ = the viscosity of the fuel.

The form of this function depends on the "shape" of the jet, but for jets of the usual type can be represented by a curve rising

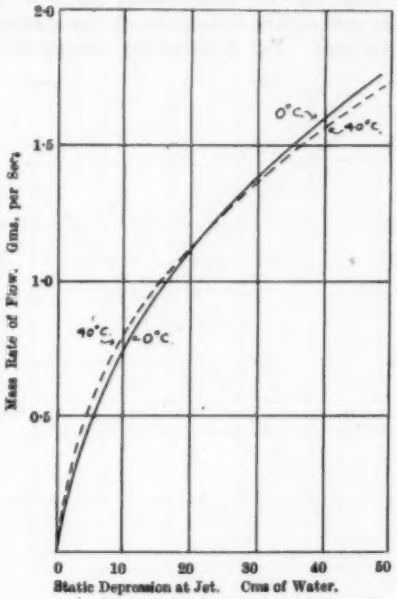


FIG. 4.

CHANGE IN MASS RATE OF FLOW OF PETROL K WITH TEMPERATURE. NO. 110 ZENITH JET.

steeply from the origin and rapidly becoming practically horizontal (Fig. 3). This implies that for large values of $vl\rho/\mu$, (Reynold's number), *i.e.* for large velocities or jet diameters, or for small kinematic viscosities, the influence of viscosity is negligible. With smaller values of $vl\rho/\mu$ corresponding to the steeply rising portion of the curve the effect of viscosity may be appreciable, particularly with such relatively viscous fluids as ethyl alcohol.

The form of the curve, C=f ($vl\rho/\mu$), and the manner in which density and viscosity vary with temperature, are responsible for

the interesting fact that increasing the temperature may increase the mass rate of flow of fuel at low heads and low rates of flow; whereas, at high rates of flow, increasing the temperature may decrease the mass rate of flow. At low rates of flow the predominating influence is that of viscosity; at high rates that of density. This is shown in Fig. 4, which gives the flow of petrol K through a No. 110 Zenith jet under static heads up to 50 cm. of water. It will be noted that over the temperature range 0° to 40° C. the difference in the rate of flow is very small, the maximum variation being only 5 per cent. Fig. 5 shows two corresponding curves for

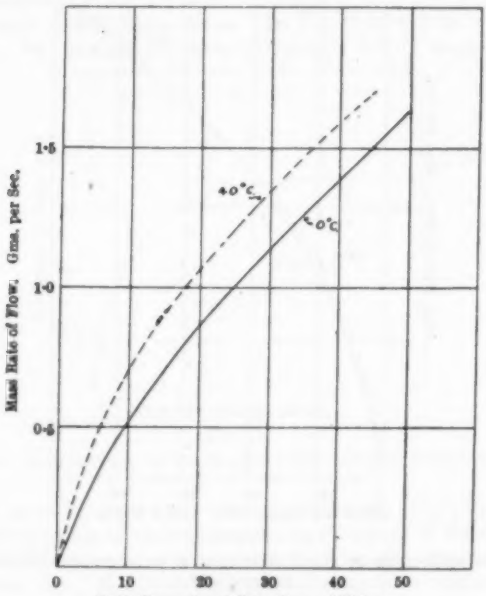


FIG. 5.

CHANGE IN MASS RATE OF FLOW OF ETHYL ALCOHOL WITH TEMPERATURE. NO. 110 ZENITH JET.

ethyl alcohol. In this instance the effect of viscosity is appreciable, the maximum increase in the mass rate of flow being about 30 per cent. for a rise of temperature from 0° C. to 40° C.

The existence of substantial differences between the viscosities and densities of different fuels is responsible, also for the characteristic manner in which each responds to changes in suction at

the jet. This is shown in Fig. 6, in which are grouped together the mass rates of flow of five fuels of varying characteristics. It will be seen that whereas the mass rates of flow of ethyl alcohol and the vaporising spirit are identical at a depression of 45 cms. of water, the rate of flow of the Alcohol is about 10 per cent. lower than that of the vaporising spirit at a depression of 15 cms.

It is clear from the above that the effect of fuel viscosity on the flow through carburettor jets, though usually small, is by no means

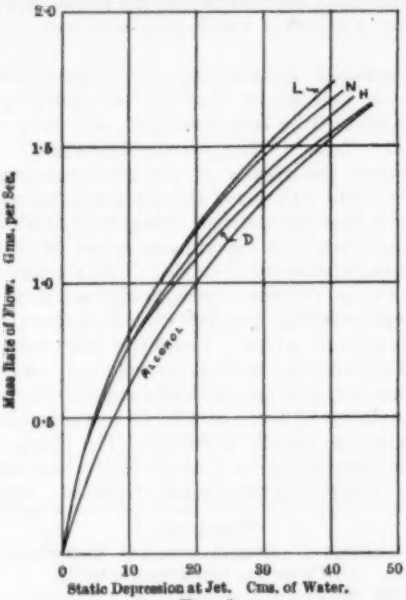


FIG. 6.

MASS RATE OF FLOW OF VARIOUS FUELS AT 20° C. NO. 110 ZENITH JET.

negligible, and therefore of considerable interest in the carburation problem. The effect is naturally greater, the greater the length of the jet in relation to its diameter.

VISCOSITY OF OILS AT HIGH TEMPERATURES.

The experimental work was carried out by means of a viscometer specially constructed from the design recommended by Bingham (Fluidity and Plasticity, p. 76 *et seq.*). The instrument, which is described in an appendix to this paper, embodies all the improvements found advantageous by Bingham in the course of

his researches on viscosity. The instrument is convenient and highly accurate, and with the experimental method adopted allows viscosities to be measured in absolute units over a wide temperature range.

The viscosities of oils S, T, V, W, Castor Oil and Special Oils Nos. 2 and 3, were measured over the temperature range 10°–250° C. The first five of these were samples taken from sealed tins or drums bought in the ordinary way of commerce in 1923, while the so-called "special oils" were experimental blends supplied for our examination, as a result of which they were never offered to the public.

Effect of Continued Heating on Viscosity—Preliminary Heat Treatment.—It is well known that the physical properties of oils are frequently affected by heat treatment, and that unless suitable precautions are taken "temperature-hysteresis" effects may seriously influence the results of viscosity measurements. Preliminary experiments with one of the oils used for the present investigations showed that the viscosity changed to such an extent with continued heating that the experiments would be of little value if the oil could not be rendered "stable." After considerable experiment the following procedure was finally adopted: The bath temperature was maintained at 200° C., the viscometer was inserted and the oil under test added. Viscosities were then measured at intervals, and systematic experiments were only commenced when the viscosity was found to be practically steady. To obtain stability continued heating for 25 hours at 200° C. was sometimes necessary, though 15 hours was usually sufficient. The changes of viscosity at atmospheric temperature as a result of the heat treatment were also recorded. The results are given in Table VI. Fig. 7 shows the

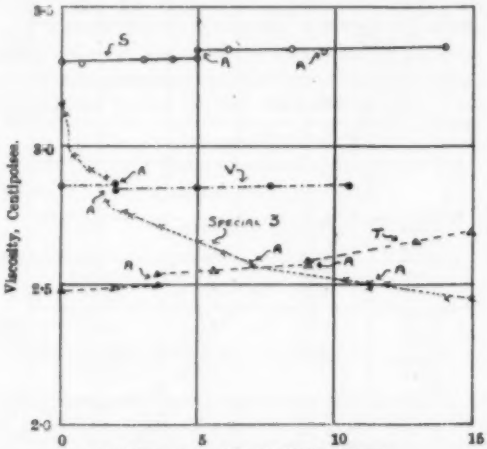
TABLE VI.

Change of viscosity with heat treatment.

(Oil heated in viscometer in bath.)

Oil.	Time of heating at 200° C. Hrs.	Viscosity in centipoises. 200° C. Start.	200° C. Finish.	25° C. Start.	25° C. Finish.	Percentage change in viscosity. 200° C.	25° C.
S	14	3·29	3·35	537	1000	1·8% increase	86% increase
T	15½	2·47	2·698	550	890	9·3% increase	62% increase
Special Oil No. 3 ..	15½	3·164	2·453	1000	422	35% decrease	58% decrease
W	8½	1·26	1·26	246	230	No change	6·5% decrease
Castor ..	11½	2·815	2·926	407	944	4·0% increase	132% increase
V	11½	1·860	1·865	—	—	0·3% increase	—

nature of some of the changes graphically. It will be noted that Special Oil No. 3 showed a continuous decrease of viscosity on heating. In this instance about 25 hours' continuous heating was required to produce approximate stability. In the case of oil T, the viscosity of which increased on heating, a heating period of about 20 hours was required. A similar increase occurred with castor oil. With oils V and W the effect of heating was negligible; with S the effect of heating on the viscosity at 200° C. was very small, though at atmospheric temperature the effect was appreciable.



("A" denotes interval of about 19 hours during which oil was at air temperature.)

FIG. 7.

EFFECT OF CONTINUED HEATING AT 200° C. ON VISCOSITY OF OILS.

Change of Viscosity with Temperature.—After the preliminary heat treatment noted above, the temperature of the bath was raised to 250° C., and viscosities were measured as the temperature was allowed to fall. Check readings at 200° C. served to show whether the oil had undergone any further change by heating to 250° C. In most cases the change, if any, was small. The temperature range down to atmospheric temperature was then explored, at first with the Bingham viscometer alone, and later for some of the oils with a Michell viscometer at temperatures below 100° C.

For the sake of brevity the results are not given in detail, but are plotted semi-logarithmically in Fig. 8. The experimental points are not shown, as in practically all cases they fall on the curves within the breadth of the line. The results for oils T, V and Castor

Oil are too close to be always represented clearly by separate curves, and are therefore shown in this and in succeeding figures sometimes by a single line. The differences in viscosity can be seen from Table VII., in which the viscosities of all the oils at definite temperatures are grouped together.

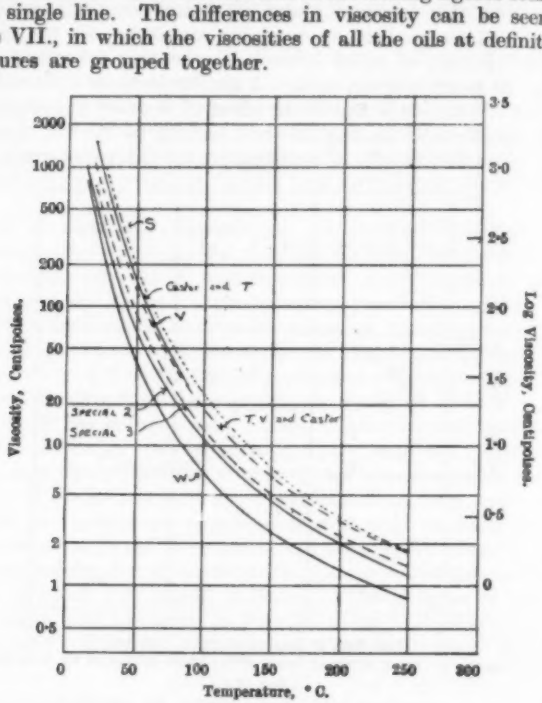


FIG. 8.

VISCOSITIES OF LUBRICATING OILS AT TEMPERATURES UP TO 250° C. SEMI-LOGARITHMIC SCALE.

TABLE VII.

Viscosities of lubricating oils.

Temp. °C.	20	30	40	50	60	80	100	150	200	250
Oil.	Viscosity in centipoises—Bingham viscometer.									
S ..	1380	708	363	204	119	59	25·24	7·546	3·37	1·852
Castor ..	1320	684	343	158·5	91·2	41·2	19·46	6·457	3·109	1·794
T ..	1259	603	285	141·3	83·2	39·36	19·78	6·237	3·015	1·778
V ..	881	448	234	133·0	81·3	37·03	19·17	6·59	2·921	1·73
Special Oil No. 3 ..	700	316	166	96·6	61·0	25·7	13·42	4·792	2·37	1·413
Special Oil No. 2 ..	507	219	120	72·44	46·24	21·38	11·48	4·22	2·138	1·245
W ..	355	150	80	47·86	29·2	12·92	7·369	2·541	1·281	0·7712

This table is worthy of study. At the lower temperatures the viscosity of an oil is approximately halved for an increase of 10° C. At the higher temperature the viscosity is about halved for an increase of 50° C. The viscosities of all the oils are of the order of one centipoise in the vicinity of 250° C.—*i.e.*, they are then about as fluid as water at ordinary temperatures.

From the form of the curves in Fig. 8 it will be seen that over a wide temperature range there is little evidence of characteristic differences in the nature of the viscosity-temperature variation for different oils. The log-viscosity temperature curves are roughly parallel and almost non-intersecting. If the curves were accurately parallel then the ratios of the viscosities of two oils would be the same at all temperatures and the ratios of the viscosities at two given temperatures would be the same for all oils. These ratios

TABLE VIII.

Ratios of viscosities.

(Bingham Viscometer.)

Oil.	$\eta 50$	$\eta 150$	$\eta 250$	$\frac{\eta 50}{\eta 150}$	$\frac{\eta 50}{\eta 250}$
S	204	7·546	1·852	27·0	110
Castor	158·5	6·457	1·794	24·5	88·4
T	141·3	6·237	1·778	22·7	79·5
V	133	6·59	1·73	20·19	76·9
Special Oil No. 3	96·6	4·792	1·413	20·2	68·4
„ „ No. 2	72·44	4·22	1·245	17·2	58·2
W	47·86	2·541	0·7712	18·8	62·0

are not equal, however, as is shown in Table VIII., where the ratios $\mu 50/\mu 150$ and $\mu 50/\mu 250$ are tabulated. The former ratio varies from 27 for the most viscous oil to 19 for the least viscous oil, the latter ratio varying similarly from 110 to 62. It has frequently been stated that all oils approximate in viscosity at 400 to 500° Fah. This statement is correct in the sense that the differences in viscosity are small in absolute amount, but is misleading in that it ignores the fact, made clear from Table VIII., that the ratio of the viscosities of two oils decreases only slowly as the temperature increases.

Change of Density with Temperature.

In the course of the investigations, the densities of these seven oils were measured by the displacement method over the temperature range 10° C. to 250° C. It was found that, with the exception of castor oil and oil T., all the oils have linear changes of density with temperature. Densities at 10 degree temperature intervals, and the coefficients of density variation are tabulated in Tables IX. and X.

TABLE IX.

Lubricating oils. Temperature—density.

Temp. °C.	20	30	40	50	60	80	100	150	200	250
Oil.	Density, gms./c.c.									
S ..	0·894	0·888	0·882	0·876	0·87	0·857	0·845	0·815	0·785	0·752
Castor ..	0·961	0·954	0·947	0·940	0·933	0·918	0·904	0·868	0·835	0·804
T ..	0·956	0·950	0·943	0·936	0·930	0·916	0·902	0·868	0·835	0·804
V ..	0·889	0·883	0·876	0·870	0·864	0·852	0·840	0·810	0·780	0·750
Special Oil. Nos. 2 & 3 ..	0·932	0·926	0·919	0·913	0·907	0·895	0·883	0·852	0·821	0·790
W ..	0·924	0·918	0·912	0·905	0·899	0·886	0·874	0·842	0·810	0·780

TABLE X.

Lubricating oils. Formulæ for density variation with temperature.

Oil.	Formula for density variation with temperature.
S	$\Delta/\Delta_0 = 1 - 0{\cdot}608\ (T/1000)$
Castor	$\Delta/\Delta_0 = 1 - 0{\cdot}6999\ (T/1000) + 0{\cdot}1108\ (T/1000)^2$
T	$\Delta/\Delta_0 = 1 - 0{\cdot}6753\ (T/1000) + 0{\cdot}04692\ (T/1000)^2$
V	$\Delta/\Delta_0 = 1 - 0{\cdot}604\ (T/1000)$
Special Oils Nos. 2 & 3 ..	$\Delta/\Delta_0 = 1 - 0{\cdot}616\ (T/1000)$
W	$\Delta/\Delta_0 = 1 - 0{\cdot}628\ (T/1000)$

Δ = density at T°C. Δ_0 = density at 0°C.

Formulæ for Viscosity-Temperature Variations.

In practical problems involving the viscous flow of oils and other liquids, it is often necessary to know, at least approximately, the viscosity of the fluid concerned at a specified temperature which is completely outside the range for which viscosity data are available. When this is the case, recourse must be had to some suitable formula, or graphical method, which will allow the known results to be extrapolated with reasonable accuracy. When this work was begun, no such method appeared to be available for use with oils. Recently, several methods have been suggested, perhaps the most elegant being those in which the logarithm of the viscosity is plotted against the logarithm of the temperature or against the reciprocal of the absolute temperature. Reference may also be made to a chart in Vol. II. of the International Critical Tables (p. 147) which allows straight line extrapolation of viscosity data for temperatures up to 150°C. In the present paper a different method is adopted depending on the use of fractional powers of the fluidity. This is in line with the modern attempts of Batschinski, Macleod, and others to trace systematic relations between fluidity and "free molecular volume." According to these views, the fluidity of a liquid depends on the "free space" available for the motion of the molecules. Macleod (Trans. Far. Soc., July, 1923) assumes that the fluidity is proportional to a power of the

free molecular volume and finds for many liquids that the index is unity. Since the free molecular volume is approximately a linear function of temperature, it follows, if the above relations were general, that some power of the fluidity should be a linear function of temperature. Bingham, in fact, has shown that for a large number of liquids, the variation of fluidity with temperature follows very nearly a linear law, the curvature being much less

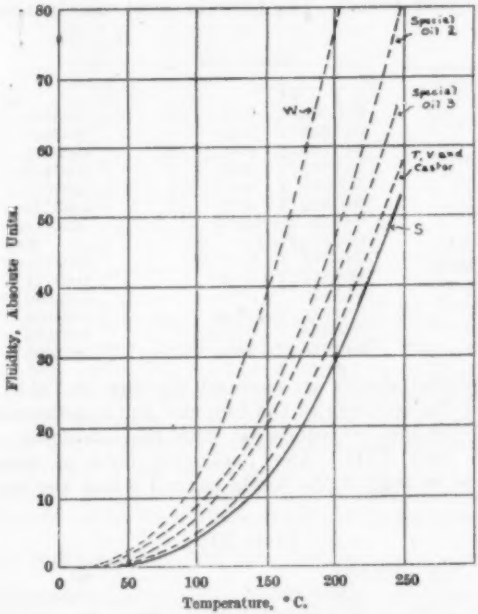


FIG. 9.

FLUIDITY-TEMPERATURE RELATIONS FOR LUBRICATING OILS.

than that of the corresponding viscosity curves. In the case of complex substances such as lubricating oils, where the viscosity is probably very much affected by varying degrees of chemical association, there is no reason to expect the existence of relations of such simplicity as those found by Bingham, Macleod, and others for mobile liquids over a limited temperature range. From Fig. 9, in which the fluidities of the oils referred to above are plotted against temperature, it will be seen that the linear fluidity-

temperature relation suggested by Bingham for "ideal" fluids, certainly does not hold for lubricating oils. In Figs. 10 and 11, the square roots and cube roots of the fluidities are plotted against temperature, and it will be noted that the former gives linear relations in the region of high temperatures and high fluidities, while the latter gives linear relations at low temperatures and low fluidities. A point of interest is that the $\phi^{\frac{1}{3}}$ curves if produced, would cut the temperature axis in the region of the figures usually given for "cold tests." The formulæ most closely representing

TABLE XI.

Oil.	$\phi^{\frac{1}{2}}$	$\phi^{\frac{1}{3}}$
S	$=\frac{0{\cdot}01545\ T+0{\cdot}044}{0{\cdot}01545\ (T+2{\cdot}85)}$	$=\frac{0{\cdot}03645\ T-1{\cdot}787}{0{\cdot}03645\ (T-49)}$
Castor oil	$=\frac{0{\cdot}01712\ T+0{\cdot}011}{0{\cdot}01712\ (T+0{\cdot}64)}$	$=\frac{0{\cdot}03442\ T-1{\cdot}185}{0{\cdot}03442\ (T-34{\cdot}4)}$
T	$=\frac{0{\cdot}01659\ T+0{\cdot}057}{0{\cdot}01659\ (T+3{\cdot}44)}$	$=\frac{0{\cdot}03616\ T-1{\cdot}426}{0{\cdot}03616\ (T-40{\cdot}4)}$
V	$=\frac{0{\cdot}0153\ T+0{\cdot}1685}{0{\cdot}0153\ (T+11)}$	Not carried above 200° C.
Special Oil No. 3 ..	$=\frac{0{\cdot}01813\ T+0{\cdot}14}{0{\cdot}01813\ (T+5{\cdot}74)}$	$=\frac{0{\cdot}03751\ T-1{\cdot}027}{0{\cdot}03751\ (T-27{\cdot}4)}$
Special Oil No. 2 ..	$=\frac{0{\cdot}01833\ T+0{\cdot}2}{0{\cdot}01833\ (T+10{\cdot}9)}$	$=\frac{0{\cdot}04059\ T-1{\cdot}087}{0{\cdot}04059\ (T-26{\cdot}8)}$
W	$=\frac{0{\cdot}02166\ T+0{\cdot}219}{0{\cdot}02166\ (T+10{\cdot}1)}$	$=\frac{0{\cdot}05006\ T-1{\cdot}115}{0{\cdot}05006\ (T-22{\cdot}3)}$

the experimental results are grouped together in Table XI. As examples of the accuracy of the formulæ, the experimental results for two of the oils are compared with the calculated values in Tables XII. and XIII. The horizontal lines in these tables are intended to suggest the limits beyond which the two sets of

TABLE XII.

Oil.	Temp. °C.	$\phi^{\frac{1}{3}}$ Measured.	$\phi^{\frac{1}{3}}$ Calculated $\phi^{\frac{1}{3}}=\cdot05006T-1{\cdot}115$	% Error.	$\phi^{\frac{1}{3}}$ Measured.	$\phi^{\frac{1}{3}}$ Calculated $\phi^{\frac{1}{3}}=\cdot02166T+\cdot219$	% Error.
	250	11·39	11·395	Nil	—	—	—
	240	10·82	10·892	+0·7	—	—	—
	220	9·94	9·895	−0·46	—	—	—
	200	8·835	8·897	+0·7	—	—	—
	180	7·886	7·897	+0·2	—	—	—
	160	6·808	6·894	+1·3	—	—	—
W	140	5·701	5·893	+3·4	3·191	3·251	+1·9
	120	4·657	4·893	+5·1	2·787	2·818	+1·1
	100	—	—	—	2·385	2·385	Nil
	80	—	—	—	1·978	1·952	−0·35
	61	—	—	—	1·513	1·540	+1·8
	41	—	—	—	1·079	1·107	+2·5
	13	—	—	—	0·509	0·5005	−0·7

TABLE XIII.

Comparison of measured and calculated values of $\phi^{\frac{1}{3}}$ and $\phi^{\frac{1}{4}}$.

Oil.	Temp. °C.	$\phi^{\frac{1}{3}}$ Measured.	$\phi^{\frac{1}{3}}$ Calculated $\phi^{\frac{1}{3}}=\cdot03751T-1\cdot027$	% Error.	$\phi^{\frac{1}{4}}$ Measured.	$\phi^{\frac{1}{4}}$ Calculated $\phi^{\frac{1}{4}}=\cdot01813T+\cdot14$	% Error.
	240	7·985	7·974	−0·14	—	—	—
	230	7·645	7·559	−0·62	—	—	—
	220	7·259	7·223	−0·49	—	—	—
	210	6·869	6·848	−0·30	—	—	—
	200	6·495	6·479	−0·23	—	—	—
	190	6·12	6·100	−0·35	—	—	—
	180	5·742	5·724	−0·30	—	—	—
	160	4·954	4·974	+0·40	2·906	3·041	4·7
Special	150	4·568	4·599	+0·70	2·752	2·86	4·0
Oil	140	4·185	4·223	+0·90	2·597	2·678	3·1
No. 3	130	3·796	3·815	+0·50	2·433	2·497	2·7
	120	3·443	3·474	+0·90	2·280	2·316	1·6
	100	2·729	2·724	−0·18	1·953	1·953	Nil
	90	2·359	2·348	−0·49	1·772	1·771	−0·07
	82·5	2·071	2·067	−0·18	1·626	1·636	+0·7
	55·0	1·13	1·036	−8·36	1·085	1·137	+4·7
	30·5	—	—	—	0·679	0·693	+2·1
	22·6	—	—	—	0·549	0·550	+1·9

formulæ cease to apply with sufficient accuracy. The agreement is, on the whole, very good. The linear $\phi^{\frac{1}{3}}$ rule (ϕ=fluidity) appears to hold sufficiently well for fluidities up to about 30 or 40. The linear $\phi^{\frac{1}{4}}$ rule can be applied from fluidities of 80 down to about 10. In the overlapping region either formula can be used, a fact which is convenient for extrapolation. With fluidities above 80 or 100, a linear ϕ rule would probably apply.

The fact that $\phi^{\frac{1}{3}}$ is a linear function of temperature for fluidities below 30 or 40 shows that within those limits, the viscosity of an oil can be represented by the formula $\mu=\frac{1}{(AT+B)^3}$ where the constants A and B are the same as those given for $\phi^{\frac{1}{3}}$ in Table XI. This expression is readily converted to the form of Slotte's well-known equation $\mu_t=\frac{M_0}{(1+bT)^n}$, but is less general, and more convenient, in that the index n is a whole number. In the whole number form of the equation, calculation can readily be carried out by means of tables of reciprocals and cubes or cube roots, whereas if the index is a number like 1.543, the value given by Thorpe and Rodger for water, tedious logarithmic calculations have to be performed involving increased risk of error. It should be noted that the range of fluidities up to 30 or 40 (or viscosities down to 3 or 2.5 centipoises) over which the $\phi^{\frac{1}{3}}$ formula is applic-

able, is sufficient to cover the viscosities of lubricating oils over a temperature range extending to at least 150, and in most cases 200° C.

From the foregoing, the necessary procedure for deriving viscosities at high temperatures from those at low temperatures becomes obvious. The most simple method is to plot the low

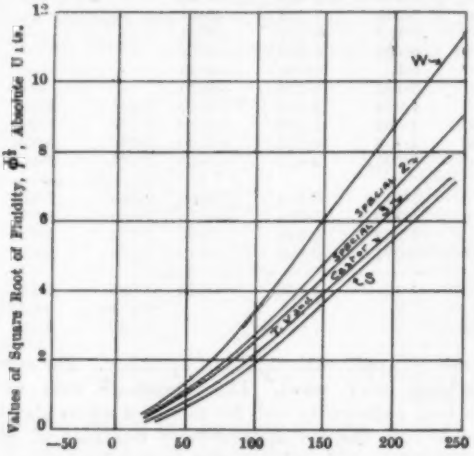


FIG. 10.

$\phi^{\frac{1}{2}}$—TEMPERATURE RELATIONS FOR LUBRICATING OILS.

temperature $\phi^{\frac{1}{2}}$ and $\phi^{\frac{1}{3}}$ figures for the oil in question and lay the extrapolated curves evenly between those of Figs. 10 and 11. This method has been used for obtaining the viscosities at high temperatures of various oils whose viscosities at low temperatures

TABLE XIV.

Viscosities of lubricating oils.

Temp. °C.	20	30	40	50	60	80	100	150	200	250
Oil.	Viscosities in centipoises—Michell Viscometer. (No preliminary heat treatment.)							(Extrapolated.)		
B.B. ..	589	275·4	135	72·44	44·67	20·0	10·0	3·802	1·995	1·189
Special Oil No. 5 ..	63·8	33·9	20·4	13·65	10·0	5·62	3·39	1·48	0·851	0·603
Special Oil No. 6 ..	178	85·1	46·8	28·2	17·8	8·71	4·62	1·82	1·0	0·631
Special Oil No. 7 ..	427	191	100	56·2	34·3	16·6	7·59	2·65	1·32	0·794
Special Oil No. 8 ..	251	126	65·3	40·0	24·6	11·5	6·0	2·14	1·18	0·733

were measured by Michell viscometer with the results given in Table XIV., the extrapolated values being given in the last three columns of the table. In Fig. 12, the logarithm of the viscosity and the cube root of the fluidity are plotted against temperature, and it will be seen that in this case as in the former, the $\phi^{\frac{1}{3}}$ curves are linear over the low temperature range. The experimental

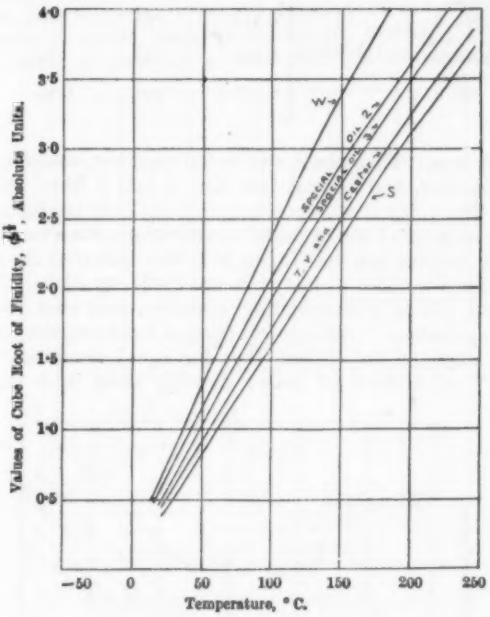


FIG. 11.

$\phi^{\frac{1}{3}}$ TEMPERATURE RELATIONS FOR LUBRICATING OILS.

points are shown, to give an idea of the order of accuracy obtainable with the Michell viscometer. The changes in viscosity at 25° C. of four of these oils, after heating in covered glass beakers at 250° C. for 11½ hours, are given in Table XV. It will be noted that oil No. 8 became nine times as viscous as a result of heating.

In view of the relations suggested above it is interesting to examine the curves obtained by plotting some power of the fluidity of various oils against the specific volume, as in Fig. 13. With this method of plotting, we note that the curves tend to fall in clearly

TABLE XV.

Change in viscosity with heat treatment.

(Oils heated in covered glass beakers.)

Oil.	Time of heating at 250° C.	Density at 20° C.	Viscosity in centipoises at 25° C. Start.	Finish.	Percentage change in viscosity.
Special Oil No. 5 (light motor)	11½ hrs.	0·904	46·8	81·3	74% increase
Special Oil No. 6 (medium motor)		0·914	129	260	101% increase
Special Oil No. 7 (heavy motor)		0·918	240	733	206% increase
Special Oil No. 8 (gear)		0·936	180	1780	890% increase

defined groups. Thus oils S and V fall together, castor oil and oil T. fall together, and Special Oils Nos. 2 and 3 form two parallel curves. The point is of importance but can only be discussed fully with a knowledge of the chemical constitution of the various oils.

Woog (Comptes Rendus 173, pp. 387–390) finds that the molecular volumes for a number of fatty oils are distinctly higher than those of mineral oils of corresponding viscosity, and that for mineral oils the "greasiness" runs closely parallel to the molecular volume. He thus explains the dictum that for equal viscosities the most "greasy" oil is that of lowest density, since in a homologous

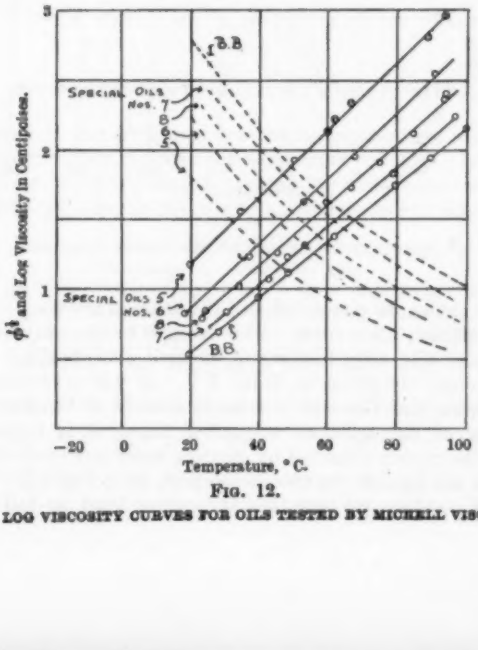


FIG. 12.

ϕ^1 AND LOG VISCOSITY CURVES FOR OILS TESTED BY MICHELL VISCOMETER.

series the viscosity increases with the molecular volume. It is, therefore, clear that a study of such curves as those of Fig. 13 will help in the interpretation of the property of "oiliness." Further consideration of this subject is beyond the scope of the present paper.

Reference has already been made to the fact that over the high temperature range, there is little evidence of any characteristic variations in temperature-viscosity relations of the oils dealt with in the present paper, such as would, for example, reverse the viscosity order of two oils at two different temperatures. The

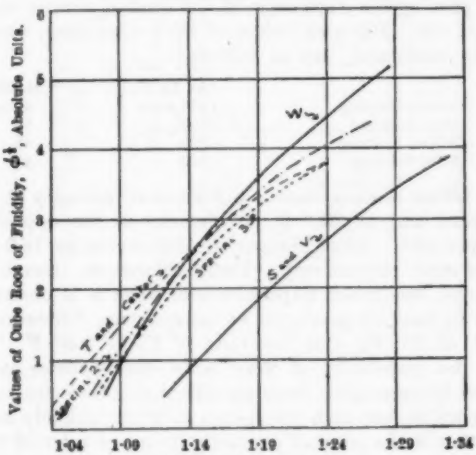


FIG. 13.

$\phi^{\frac{1}{3}}$ SPECIFIC VOLUME RELATIONS FOR OILS.

foregoing suggests, in fact, that if oil A is more viscous than oil B at 50°C., then it is more viscous at all high temperatures. Moreover, the figures in Table VIII show that as the viscosity rises, the ratio μ low/μ high also rises. This implies that if we require higher viscosities at high temperatures, we have to accept proportionately much greater viscosities at intermediate temperatures.

These statements do not entirely exclude the possibility of the viscosity curves of different oils crossing at low temperatures. Thus Evans (Lubricating and Allied Oils, p. 28) gives viscosity curves for castor oil and a mineral oil which cross in the neighbourhood of 10°C., the former being the more viscous at higher temperatures, and the latter at lower temperatures.

More than one manufacturer has embodied this crossing of viscosity curves in attractive advertisement matter, and there is no doubt that of two good oils, the one possessing greater viscosity at high temperatures, and less viscosity at low temperatures, would be greatly preferable. Quite apart from the greater ease of starting from cold and the more effective lubrication when hot, there is the general consideration of safety under overload and emergency. But from the great bulk of experimental evidence underlying this paper it is to be doubted whether any substantial crossing of the viscosity curves is to be expected. One oil blender, for example, by way of proving his contention of the crossed curves, submitted two selected oils. His own values of their viscosities, which have been closely confirmed, are as follows:—

		At 70° F.	At 200° F.
Oil X.	Before heating	1133 secs. ..	49 secs.
	After heating	1204 „ ..	50 „
Oil Y.	Before heating	1221 „ ..	45 „
	After heating	1445 „ ..	47 „

These oils, before heating, show a difference of viscosity at 70° Fah. of 7·5 per cent. and at 200° F., a difference in the opposite direction of 8·5 per cent. After heating, the differences are 18·2 per cent. and 6·2 per cent. respectively. These differences, though striking at first glance, lose much impressiveness when it is observed that they could be entirely produced by temperature differences of less than 3° F. at 70° F., and less than 6° F. at 200° F. There is, of course, the possibility of very wide discrepancies at high or at very low temperatures between oils that otherwise may seem to be comparable, but such divergence may not unlikely arise from decomposition or the onset of plasticity in one or more of the ingredients. If this view is correct, and it is supported by theory and results on liquids other than oils, it would appear that the occasional slight crossing of viscosity curves should not be given emphatic notice. It is perhaps unnecessary to point out that the selection of the oils X and Y was more studied than impartial; as a matter of fact, the two oils hardly bear comparison. Oil Y for instance, during 15 hours heating in an open tube at 200°C. showed progressive increase of viscosity up to 58·5 per cent. above its original value, whereas oil X under the same heat treatment showed an increase of only 5·3 per cent.

A New Viscosity Characteristic.

It has already been mentioned in the introductory chapter that the usual viscosity temperature curve is geometrically ill-conditioned. At low temperatures the slightest variation of temperature produces enormous variations in viscosity, while at high temperatures

the viscosity appears to be almost immune to temperature effects. Fluidity curves are open to similar objections in that they obscure viscosity variations at low temperatures and exaggerate them at high temperatures, whilst logarithmic plotting, as is well known, tends to close up the scale and mask the effects of characteristic differences as well as the extent of experimental errors. In view of these geometrical blemishes an attempt has been made to construct a new characteristic free from the defects of the ordinary curve in daily use. This characteristic is constructed by plotting

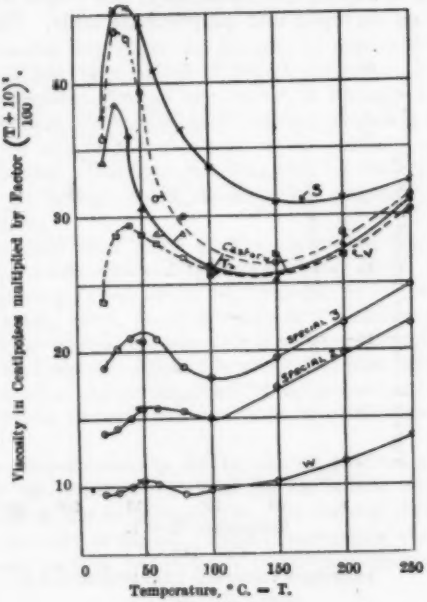


FIG. 14.

PROPOSED VISCOSITY CHARACTERISTICS.

on a temperature base, as in Fig. 14, the viscosity multiplied by $\left(\frac{T+10}{100}\right)^3$, where T is temperature in degrees centigrade. This temperature multiplier can be easily tabulated ready for use with all oils.

The significance of this characteristic curve deserves close attention. If an oil possessed fluidity varying according to the law

$\phi^1 = A(10+T)$, the characteristic in Fig. 14 would become a horizontal straight line, and therefore the ordinates of the various curves in Fig. 14 represent the ratio of the viscosity of each oil to that of a hypothetical "standard" oil whose fluidity varies with temperature in the manner just indicated. The arbitrary choice of the vertex of the cubic curve, at −10°C., is no doubt largely responsible for the particular form of distortion of the characteristics, but it would appear that similar distortion is inevitable with the use of any other simple multiplying factor, or any attempt to express the viscosities of oils over a wide temperature range on an open and proportional scale. This is shown

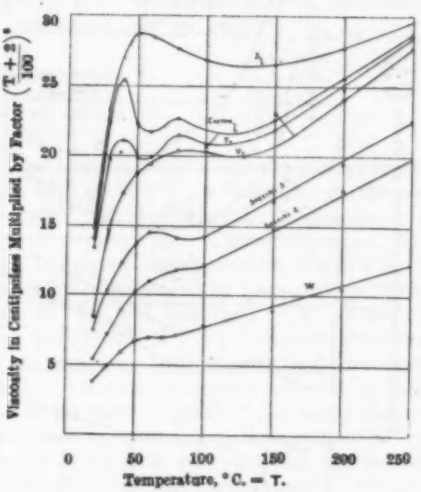


FIG. 14A.

PROPOSED VISCOSITY CHARACTERISTICS

very clearly in Fig. 14A which is plotted with the vertex at −2° C., *i.e.*, the ordinates are $\mu\left(\frac{T+2}{100}\right)^3$ The advantages of the characteristics are threefold. Firstly, they show ratios of viscosities of different oils at the same temperature at a glance; secondly, they show more clearly than any of the preceding curves the extent of difference in the characteristic viscosity-temperature variation of different oils; thirdly, they expose the extent of experimental errors and local irregularities in the curves. It is clear from the form of the curves of oils V, T and castor

oil, that the viscosity of the first-named changes less with temperature than those of the other two, a fact which is obscured with the other methods of plotting mentioned in the paper. The apparent slight reversal of the experimental values for these three oils in the neighbourhood of 150° C. is most probably due to slight incompleteness in "stabilisation." As already mentioned, this new "characteristic" is not offered as a final recommendation for universal application but rather as a starting point from which discussion may proceed.

The Air Bubble Viscometer.

It was intended originally to include in this section a brief discussion of a few viscometers of recent invention, little known to general workers. But as the paper is already inordinately long, this intention has been abandoned and instead, a few results are included on one of the oldest of all viscometers, namely the bubble in the tube. This type has been used for many years in the varnish and oil industries and is therefore presumably of some practical utility.

In order to gain clear ideas on the underlying factors in this "instrument" some qualitative experiments were made with bubbles of mercury in oil, air in oil, hydrogen in oil, water in oil, oil in water, air in water, petrol in water and petrol in sugar-water solutions. These were of considerable interest and merit the study of physicists and mathematicians interested in pure science. They showed among other things the effects of the viscosity of the bubble, of surface tension, of turbulent flow and of relative densities and viscosities.

From these experiments it was apparent, that from a practical point of view the principal factors in the air bubble viscometer are the tube diameter, the tube inclination, the density of the oil under test and the viscosity of the oil. These observations were confirmed by dimensional analysis which leads to an expression of the form

$$V = \frac{gr^2(\rho_1 - \rho_2)}{\mu_1} K$$

where V = the speed of the bubble
r = the radius of the tube
μ_1 = the viscosity of the liquid
ρ_1 = the density of the liquid
ρ_2 = the density of the bubble, usually less than ρ_1

and K is a function of non-dimensional fractions composed of the variables already mentioned together with the viscosity of the bubble and the surface tension of the liquid at the bubble surface.

Experiments were then made in order to test this relation and

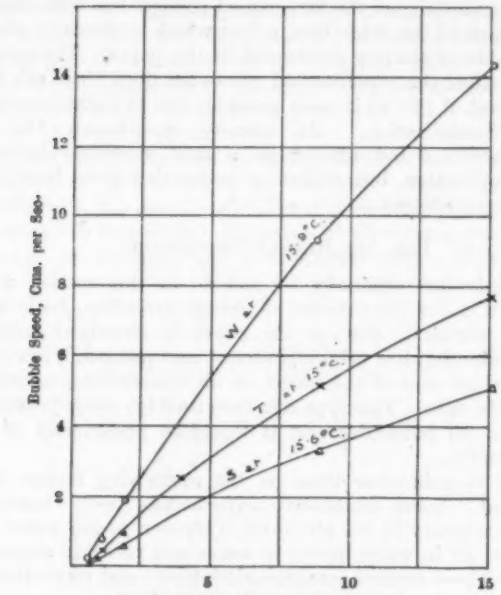


FIG. 15.

AIR-BUBBLE SPEEDS IN TUBES OF DIFFERENT DIAMETERS.

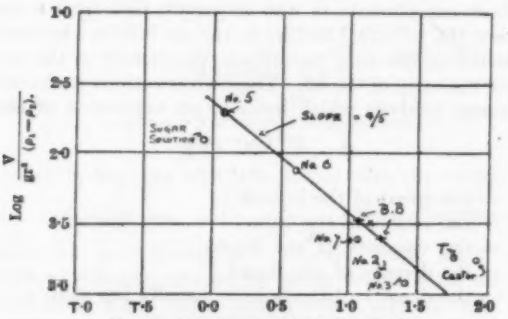


FIG. 16.

SPEED OF AIR BUBBLES IN VARIOUS LIQUIDS,
Log $V/gr^2(\rho_1-\rho_2)$ plotted against log μ.

the results are shown in Figs. 15 and 16. The effects of tube slope are shown in Fig. 17. These diagrams show:—

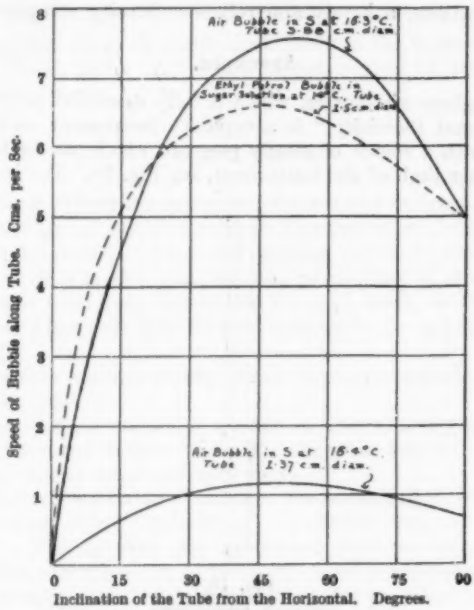


FIG. 17.

SPEED OF BUBBLES IN INCLINED TUBES.

(*a*) That the speed of the bubble is approximately proportional to the square of the tube diameter so long as this diameter exceeds 6 mm.

(*b*) That the speed of the bubble is approximately inversely as the viscosity of the liquid though apparently an expression of the form $V \propto \frac{1}{\mu 0{\cdot}8}$ is more exact.

(*c*) The slope of the tube greatly affects the speed of the bubble which is a maximum at about 50° to the horizontal.

As a collateral experiment various bubble lengths in various tubes were tried and it was found that the speed was unaffected by the length of the bubble so long as this exceeded about 1·5 diameters of the tube.

In the main these experiments agree with those of Barr and of Faust conducted from rather a different point of view, and it may be concluded that the bubble-in-tube viscometer is, within common sense limitations, a handy and reliable viscosity comparator.

Appendix.

The Bingham viscometer, which is fully described in Bingham's "Fludity and Plasticity," is a capillary instrument used in conjunction with a source of steady pressure which can be turned at will to either limb of the instrument, see Fig. 18. The instrument

Fig. 18.
BINGHAM VISCOMETER.

was inserted in an electrically heated bath of castor oil, mechanically stirred to maintain uniformity of temperature. A small electric bulb in the oil supplied the necessary illumination.

The constants of the instrument were determined by calibrating the instrument with 60 per cent. and 40 per cent. sugar solutions both before and after the series of experiments. The two sets of calibration were practically identical, showing that the instrument had not been affected by use. The viscosities of sugar solutions are those given by Bingham (Fluidity and Plasticity, p. 341). (A more convenient set of data is now available in B.E.S.A. publication No. 188—1923). Check experiments with water showed that the instrument was sufficiently accurate for low viscosities as well as for the higher viscosities. For some reasons it would have been advantageous to use two instruments, one for low and the other for high viscosities, but the sacrifice of these advan-

tages was more than compensated by the convenience of using one instrument only over the whole temperature range.

Acknowledgment.

The authors desire to thank the Council of the Research Association of British Motor and Allied Manufacturers for permission to publish this paper.

DISCUSSION.

Dr. F. B. Thole congratulated the authors on having extended our knowledge of viscosity-temperature curves of lubricating oils into the relatively unexplored regions beyond 150° C. The absence of data in this area was due to the fact that commercial instruments were quite unsuitable for such work, as the times of flow were so low that they bore no relation to the actual viscosities of the oils.

Two points emerge clearly from the experimental results on lubricating oils:—

(1) There is no abnormal change in the viscosity-temperature curve at elevated temperature; the course is that to be expected by extrapolation of the ordinary curve.

(2) Most oils are liable to undergo serious chemical changes when heated under the "stabilising" conditions employed in this research. The speaker was convinced that viscosity-hysteresis effects were not the cause of these increases in viscosity (or in one case a decrease, probably due to cracking) for the following reasons: (*a*) Viscosity-hysteresis effects are rarely met with in lubricating oils (except the very heavy ones), and then they quite disappear at temperatures of about 100° F.; (*b*) the effect of heating is to diminish viscosity when this is due to hysteresis effects; (*c*) where no chemical change has occurred it is possible always to bring the oil back to the same temperature that it had before heat treatment and obtain the viscosity figure which it originally had at that temperature; where chemical action such as polymerisation or oxidation has occurred the heat-treated oil has a permanently different viscosity-temperature curve at all temperatures to the original unheated oil. It would seem that heating these oils to 200° C. for some hours brings about changes similar in kind, though less in extent, to those occurring when tung oil, castor oil or linseed oil are similarly treated.

The best method of expressing viscosity results graphically has often been discussed, and it will be interesting to see if the system suggested by the authors shows general advantages over the

familiar methods. It is generally accepted that the only really useful portion of the ordinary curve is the middle section, but logarithmic functions or (to a less extent) square or cube roots are merely methods of reducing the scale, and thus minimising errors or variations which are better unconcealed. Further, small errors in reading a logarithmic or cube root curve when translated back into terms of viscosity are magnified.

The speaker agreed with the authors' point that slight crossing of viscosity curves did not indicate any material difference in the values of the oils, but cases did exist where the difference in slope of two curves was sufficiently great to indicate a really serious difference in the two oils under comparison. The SO_2-extract from certain naphthenic lubricating oils, for example, had an extremely steep curve as compared with an ordinary oil.

The insignificant influence of viscosity on the flow of motor spirits through carburettor jets was well known, as the rate of flow is far above the critical value; the discrepancy between the curves for heptane or octane and for the average petrols is due to the fact that the latter all contain relatively high proportions of naphthenes which are considerably more viscous for equal molecular weights. The viscosities of cyclohexane and of *n*-hexane at 25° C. are 0.0089 and 0.0030 respectively. (Thole, *J.C.S.*, 1914, **105**, 2004.)

Mr. E. A. Evans thought it was very strange that so few Papers on viscometry had been read before the Institution, considering that one of the very earliest Papers presented was from the National Physical Laboratory, in which reference was made to the very subject under discussion that evening. The subject was one of extraordinary importance, and a debt of gratitude was due to the authors for bringing it forward once again. Those who were associated with the commercial end of petroleum would, he felt certain, be particularly thankful to the authors who were in direct touch with people with whom commercial men were also in touch, and a word from them under such circumstances went a long way. Unfortunately, the subject of viscosity was very little understood by average motor manufacturers. They had the idea that viscosity was a perfectly simple function; that it was easily measured and that its determination was subject to a very small amount of error. They also believed that at certain temperatures all oils had the same viscosity. That, of course, was an absolute fallacy and had been known to be such for a great number of years; and if the authors had definitely issued reports to their friends in the trade on the subject he was sure the thanks of the members were due to them for doing so. There were several points in the Paper with which he desired to deal. It was stated that boundary lubrication was perhaps a little over-emphasised and that viscosity was not

sufficiently emphasised by certain people. That might be partially true. Viscosity in ideal lubrication was important, but in a motor-car with the average driver on the road it seemed to him that boundary lubrication became even more important. There were the sudden changes of pressure, and obviously a considerable amount of boundary lubrication must be obtained as manifested by the wearing of the bearings and the cylinder walls. In Fig. 7 the authors gave the viscosities of certain oils, but did not indicate the temperature at which they were taken. Perhaps they would be good enough to supply that information. In Fig. 8 the authors showed the comparative viscosities of certain oils against castor oil. He would like to know whether those oils were pure mineral oils or whether they were compounded with fatty oil. Further on in the Paper some curves were given to prove the accuracy of the Michell viscometer. Personally, he had made numerous trials of the Michell viscometer, and his experience had not been quite so happy as that of the authors. It might be that he had not handled the Michell viscometer quite in the right way, but the difficulty seemed to be mainly in the actual time it took for the ball to drop. Further on in the Paper the authors referred to the air-bubble viscometer. He hesitated to speak on that subject in the presence of Dr. Barr, but personally he felt that the air-bubble viscometer was not particularly accurate. He imagined that it must vary within fairly large limits through the distortion of the shape of the air-bubble when it was passing through the fluid, and also the physical characteristics of the material through which it was passing would have to be seriously considered, and the metal or material from which it emanated. Dr. Thole had suggested that the variation in viscosity was probably explained chemically. Personally, he was inclined to think that the variation was due to physical phenomena, because variations within such wide limits could be obtained simply by heat treatment. Unfortunately, he had been having a little trouble lately and had been looking into the variations of viscosity somewhat closely. Simply by heating the oil to a temperature of 80° C., and allowing it to cool, very large variations could be obtained in the viscosity at the freezing-point of water. That, of course, was a temperature considerably lower than the authors had dealt with in the Paper. If the oil was heated again and then cooled down under apparently the same conditions quite large variations occurred. Perhaps the authors could give some indication whether they had any experience of that sort of difficulty, and if so how they overcame it. He did not know whether the Paper suggested that the method of overcoming that difficulty was to maintain the oil for long periods, say, over 15 hours, at 250° C., as a practical proposition, because he was

rather afraid that from a commercial point of view it would be perfectly impossible.

Mr. C. I. Kelly said that he was afraid he was in the same difficulty as Dr. Thole in discussing the Paper, because he found it very difficult to distinguish between changes in the oil brought about by physical and chemical means; but he believed the difference in the viscosity of the authors' oils was directly due to chemical influences. He had been carrying out a good deal of work on the effect of air and oxygen on mineral oils, and found that even if the oil was enclosed in a glass vessel so that on heating, the oil expanded into a capillary tube, thereby overcoming the influence of convection currents on the surface, viscosity changes were still obtained due to action of the air or oxygen which was dissolved in the oil itself. He thought that had a great bearing on the viscosity changes which the authors observed when they heated the oil at 200° C. for 15 hours. The figures contained in Table XV. reminded him very strongly of what happened to oils when they were subjected to the Water's Oxidation test. The only difference between the latter and the author's experiments was that the glass beakers were covered. In the Water's Test, the oil was subjected to an elevated temperature in an aluminium dish, but the change of air at the surface of the oil was assisted by rotating the dish on a circular tray. He thought that oxidation lay at the bottom of the viscosity differences. One should not overlook the effect of prolonged heat treatment in the absence of air above the oil, or the heterogeneous compounds found in all petroleum lubricants—sulphur compounds. In the case of certain classes of lubricating oils, the sulphur compounds decomposed on heating to temperatures below 200° C. to give rise to sulphuretted hydrogen and free sulphur. It is possible that chemical changes such as this may have had something to do with the viscosity changes observed by the authors. Reference had also been made to the viscosity hysteresis of oils. His own experience was that changes were found in a very marked degree only in unrefined products and not in refined products. For instance, if fuel oil was heated to 180° F. for two hours or so and allowed to cool without any agitation at all the viscosity at 32° F., or even at a higher temperature, say 70° F., might be decreased by two-thousand seconds, but if it was stirred whilst cooling, or if the oil were allowed to stand for several days after the heat treatment the separation of paraffins or whatever might be in solution seemed to be assisted, and that increased the viscosity to the original figure. But in the case of carefully refined oils, particularly of an asphaltic base, he did not find the viscosity change was very manifest, except when one went down to very low temperatures for viscosity determinations.

In the case of paraffin base or mixed base oils, trouble would be encountered if viscosity determinations were made near to the cloud and pour points.

Dr. G. Barr said he desired to make a comment on one point dealt with at the end of the paper, viz., on the question of the change of viscosity by the heating of oils in air. He suggested that if the authors were attempting to reproduce the conditions in a bearing and the effect of those conditions on the oil, heating should be done in contact not with air but with the metals which comprise the bearing, because the effect on the oil would probably be very different. He had been particularly interested in two figures dealing with the measurements made with the Michell viscometer and with the air bubble viscometer. He thought it probable that the accuracy indicated for the Michell viscometer, to which a previous speaker had drawn attention, was possibly not as high as appeared from the look of the curve, but was explained by the characteristic, to which Dr. Thole referred, of the disappearance of experimental errors by plotting results in logs. At the same time the accuracy which the authors had obtained with the Michell viscometer was higher than he had been able to get with an instrument which he used some years ago. It had always appeared to him that the difficulty of obtaining reproducable results with a Michell viscometer was rather due to the fact that that viscometer was based possibly on an incorrect view of what took place during the fall of the ball. It was assumed that the time of fall was fixed by the time required for the oil to run into the narrow space between the ball and the cup which is delimited by the three small projections which keep the ball in place. That simple theory took no note of the resistance offered by the very minute film between the pegs and the ball. He made a rough calculation some time ago as to what the effect of the pegs would be, and concluded that it was quite conceivable that the retaining effect of the minute film of oil on the pegs was equal to the retaining effect of the oil in the whole of the cup. That did not necessarily mean that the instrument would not measure the viscosity accurately, but it did mean that the workmanship had to be of an extremely high order of accuracy, and that if there was any effect due to absorption and change of viscosity with rate of shear, the Michell viscometer would detect it and have its readings influenced by that effect. On the other hand, a capillary viscometer dealing with very much larger clearances would not indicate any such effect. The conclusions to which the authors arrived on the subject of an air bubble viscometer were, as they suggested, fairly well in agreement with those at which he (Dr. Barr) arrived in his paper of a year or two ago;

but the authors did not include in their curves any correction for the effect of surface tension on the results. Fortunately, in all oils the surface tension did not vary very widely from one oil to another, and so long as oils more or less of one class were being dealt with, the air bubble viscometer, if the diameter of the tube was of a suitable size, would give results which were fairly proportional to the viscosity. In Fig. 16, for instance, it would be observed that the point for castor oil at one end and for a sugar solution at the other came very far off the mean curve which had been drawn, and those were precisely the two substances which had different surface tensions from the remainder of the oils.

Mr. A. T. Wilford said he desired to associate himself with the remarks made by Dr. Thole, particularly in regard to the heating of oil to a temperature of 250° C. affecting its chemical character. It was only necessary to heat an oil in a tube at 250° for a short time to darken its colour.

Further, through the heat generated in a differential gear, it was possible for a lubricating oil, which normally could be poured at ordinary temperatures, to be converted into a solid mass that, literally, had to be chopped away.

These two cases were surely indications of chemical and not physical change.

In any case, he did not think that the question of viscosity at 250° had very much bearing on the lubrication of an automobile. The only part affected was the cylinder walls. If the clearances between piston and cylinder were small, boundary lubrication would occur, whilst, if the clearances were large, oil would be diluted with the fuel used.

He regarded viscosity as being merely one of the finger prints by means of which it was possible to recognise an oil which experience had proved to be a suitable lubricant.

Mr. C. Chilvers said he desired to raise one point in connection with the question of whether the change in the oil was a chemical or a physical one. He desired to ask if the authors had carried out any experiments by heating the oils for more prolonged periods at lower temperatures than 250°, say, 100° C. Would continued heating at 100° C. produce the same ultimate viscosity, even if it took a longer time than the equivalent of 15 hours at 250°?

If the change were chemical, it would probably be proceeding, though with a slower velocity, at lower temperatures and, in this case the same final product with the same ultimate viscosity would be obtained by more prolonged heating at the lower temperature.

Dr. F. B. Thole said he desired to add one further point with regard to the question of physical *versus* chemical change. If

the change was a physical one it should be possible to restore by long keeping the original viscosity, whereas if the change was a chemical one the original viscosity would not be reproduceable under any circumstances.

Mr. E. A. Evans said he was afraid that his previous remarks had been a little misunderstood. He did not question that the viscosity could not be reproduced. His interpretation of the paper was that, owing to the variations in the viscosity if the oil was heated to a temperature of 250° a constant figure could be obtained afterwards. His difficulty had been that when heating oil up to a temperature of 80° or 100° and cooling it he obtained varying figures at different rates of cooling.

Mr. D. Finlayson, in reply, said the authors were pleased to have the support of Dr. Thole in a number of their statements. They agreed with him in his remarks in regard to the uselessness of ordinary viscometers for work of the kind presented in the Paper. It was quite true, as Dr. Thole said, that carrying the curves to a higher temperature had disclosed no surprising phenomenon and had given viscosities of the order likely to be predicted by extrapolating existing curves, but prior to the work of the authors, the propriety of extrapolation was entirely suppositious. In regard to Dr. Thole's remarks on experimental errors in plotting, the authors had emphasised that point in the Paper. If logarithms of the viscosity were plotted against temperature, the scale was closed up to such an extent that experimental errors were entirely hidden and, by the unwary, quite a wrong opinion of the accuracy of the measurements might be obtained. The case was not quite the same when fluidity and the cube root of the fluidity were plotted against temperature. In plotting fluidity, the proportional error was the same as in plotting viscosity. If the cube root were plotted the proportional error became one-third. From experience the authors had found that ϕ 1/3 curves were extremely convenient in predicting the viscosity of an oil at any specified temperature when they knew the viscosity at one or two other temperatures. If the viscosity were known at one temperature only, the method adopted was to work out the fluidity, take its cube root and plot the point on a chart with a number of other ϕ 1/3 curves. If a line, passing through the experimental point, were then laid evenly among all the other ϕ 1/3 curves, it was possible to use this line to predict the viscosity at other temperatures with quite reasonable accuracy. If the viscosities at two temperatures were known, then the whole line could be laid down with much certainty. The authors were very pleased to hear Dr. Thole refer to the cause of the displacement of the fluidity specific-volume curves for petrols.

from the curves for heptane and octane. The authors would have included in Fig. 2 data for individuals of the naphthene group, had they been aware of them. If Dr. Thole had any such data, it would add greatly to the value of the Paper if he would contribute them in writing as part of the discussion. It was clear to the authors that the reason was the naphthene content, but they thought it was better to leave such a statement to the expert opinion of the members of the Institution. In reply to Mr. Evans, the viscosity referred to in Fig. 7 was the actual viscosity at 200° C. The oil was put in a viscometer and kept at that temperature, the viscosity being measured at intervals. In a few cases the oil was cooled down to room temperature and the viscosity noted. The values were given in Table VI. Mr. Evans, referring to the air bubble viscometer, had said that he did not consider the results were very accurate. That was shown by the results of the authors themselves. Their suggestion was that the instrument was merely a convenient viscosity comparator, not a viscometer. Dr. Barr had referred to the same subject at greater length. It was quite clear from the curves that other things than viscosity had an influence, and that was explained by Dr. Barr's own work. He had pointed out that the experimental points for a sugar solution and for castor oil were displaced appreciably from the curves, showing that properties other than viscosity had an influence. For rough purposes it was quite sufficient to assume that the time taken by the bubble to travel was proportional to the viscosity, but it was not accurately so. The lesson to be learnt was that if anyone desired to use a bubble viscometer he ought to calibrate it with a liquid of approximately the same character as the liquids to be tested. For instance, he ought not to calibrate an instrument for use with oils with a sugar solution. Most of the other speakers had devoted considerable time to a consideration of the subject of whether the changes in the viscosity of oils produced by heating were chemical or physical. That was a subject that was really beyond the province of the authors, who were not so much concerned with the cause as with the effect. It was quite clear in their experiments that the curves would be absolutely useless unless the oils were rendered stable to begin with, and they found that prolonged heating at 200° was quite sufficient for the purpose. That was checked by heating them subsequently to 250° and seeing that the viscosity came back to approximately the same value when the temperature fell again to 200°. The heating was done actually in the Bingham viscometer so that the oil was only exposed to the atmosphere by means of a very thin tube—practically a capillary. The authors wished to make it quite clear that the changes in viscosity produced by heating were permanent, not temporary.

After the oils had been heated for 15 hours or more, the authors found they could reproduce the results at any temperature without any difficulty

Mr. H. S. Rowell, in reply, said there were a few points calling for immediate discussion, especially that relating to the temperature of the oil between lubricated surfaces. Dr. Thole had thrown a little kindly doubt on whether 250° was a reasonable temperature even in Diesel engines or automobile engines, and stated that only a minute fraction of the oil was ever at 250° C. The whole crux of the problem was that it was this minute fraction at 250° C. which caused all the trouble. As a result of very elaborate determinations by Becker in Charlottenburg and by Gibson in Manchester and in Farnborough, there could be no doubt that in many engines the temperature of the oil film between the piston and the cylinder was of the order of 250° C. Without a definite assurance of that kind the authors' experiments would never have been carried out. Without information on the viscosities at those temperatures, and especially at the temperatures after some time of heating, it was impossible to reason on the behaviour of pistons and cylinders or to account for the curious anomalies in wearing, seizing, and so on. He thought it must be urged that the temperature was a reasonable one, and possibly in the future oil refiners and blenders would be called upon to include such a temperature in some of their specifications. With regard to the relative importance of boundary lubrication and viscosity, he was much interested in Mr. Evans' remarks, more especially as he had recently recoiled from a very intense enthusiasm for boundary lubrication. He had had the pleasure, some years ago, of collaborating with Sir William Hardy and his assistants on boundary lubrication, and at that time it appeared as though it might explain almost everything anomalous in lubrication. But the main thesis of the paper was that if the film of viscous lubricant were maintained, then boundary lubrication did not arise.

It was by no means rare to find that case-hardened steel gudgeon pins or big-end pins were blue or straw-coloured, indicating temperatures of some hundreds of degrees higher than 250. With regard to the Michell viscometer, it was very pleasant to observe the amazement which its accuracy had engendered, but he thought there were two main elements in its success. One of them was to choose a viscometer of the right size for the grade of oil being used. The viscometer was based on a mathematical calculation. All mathematical calculations were based on assumptions, and unless the assumptions were realised in the instrument, i.e., the thickness of the film, so as to get over the time difficulty as well as to allow of the annulus at the outside of the film to supply it properly,

then accuracy could not be expected. The second element which it was rather difficult to explain was the need for sifting or straining the oil. Minute particles of grit or fluff, perhaps even some colloidal formation, appeared to have a tremendous effect on the consistency of the results. If small particles in a very thin aperture were imagined, it was perfectly obvious that the flow of the oil past those solid boundaries might appear enormously more viscous. The flow of oil in a sheet was usually as the cube of the aperture; by putting a small particle in the aperture the space might be decreased by half, and so the errors in the flow of the film in the Michell viscometer were explained. The last speaker had referred to the effect of metals, which was not unknown. In all the old pocket books and recipes dating right back to Coulomb and even 200 years ago, the friction of wood on iron, of iron on iron, of brass on iron, and so on, were all given different values. It was realised then that metal on metal gave different coefficients of friction according to the metals, the state of polish and so on. More lately the contamination of the surface with an unguentous layer had been shown greatly to affect the friction.

So far as the results enabled one to form an opinion, it appeared that the molecules of the bearing metals had different attractions for the molecules of the lubricant. Taking, for instance, steel on steel, with very high local pressure, the coefficient was approximately 0·64 when perfectly clean; while with brass on brass of a similar shape a coefficient of friction as high as 0·96 was obtained. With a piece of brass and a piece of steel the arithmetical mean between the two was obtained, namely, 0·80. Similar but vastly less precise results had been found by the old millwrights in developing brass bushes round steel shafts. The remaining points could be dealt with in a written reply.

The Chairman, in moving that a very hearty vote of thanks be accorded to the authors for their most interesting paper, said as Dr. Thole had stated it went into a region which, though not entirely unexplored, was comparatively unexplored, and for that reason alone, apart from the general merits of the paper, he was sure the members would desire to accord the authors a hearty vote of thanks, particularly as the paper had given rise to such an excellent discussion.

The resolution of thanks was then put and carried by acclamation.

Continuing their reply in writing, the authors felt justified in emphasising that from the point of view of viscometry little importance could be attached to the question as to whether the changes in oils as a result of heating were physical or chemical. Clearly,

both physical and chemical changes were possible and the essential point in viscometry at various temperatures was to make the determinations when the physical or chemical changes had come to a stop. This had been done so completely in the course of the work that it had been found possible after an interval of two or three years to repeat previous determinations. At the same time it was not intended to belittle the importance of producing oils of invariable or stable characteristics and all users would welcome the efforts of the refiners in this direction. Mr. Evans had doubted the economic feasibility of stabilising oils by heat treatment, but it was open to question whether his difficulty was real. If oils are to be used under high temperature conditions, they will stabilise under those conditions, and the most important desideratum was not necessarily the preliminary stabilisation by some artificial treatment, so much as a knowledge of the results, qua viscosity, of exposure under conditions of operation. To judge from the attitude of some of the speakers, additional emphasis was necessary on the importance of high temperature viscometry, and in general the need for all-round investigation of oils in the neighbourhood of 250°-300°C. If it were a little difficult to accept these measured temperatures in water-cooled internal combustion engines, at least the recent tendencies in steam practice should prove persuasive. In many steam units by no means recent, 320°C. is common, and new developments suggest that much higher temperatures will be prevalent—if the lubricating oils prove equal to the task.

In regard to Mr. Evans' question on Fig. 8, all the oils excepting S, T, V and Castor were believed to be pure mineral oils. The differences are more clearly displayed in Fig. 13.

Dr. Thole had somewhat deprecated the importance of the viscosity of motor fuels on the ground that the rate of flow is far above the critical value. Against this must be urged that the maximum rates of fuel and air flow in automobiles were about 25 times the minimum, and at the lower rates, as shown in Figs. 4 to 6, viscosity played an important part and, therefore, special slow running systems were used.

The authors were much obliged to Dr. Thole for his information on the viscosity of cyclohexane, i.e., 0·0089 at 25°C., and for referring them to data obtained by Drapier (Bull. de Belg., 1911, p. 621). Unfortunately, information on the specific volume appeared to be very incomplete and therefore it was not possible to insert the cyclohexane graph in Fig. 2, with any precision. Taking, however, two values at 0°C. and 10°C., given in Thorpe's "Dictionary of Applied Chemistry" (Vol. V., p. 77), and extrapolating along a straight line, a curve had been computed which

deviated very markedly from the others in the diagram; whereas the curves given in Fig. 2 are almost parallel and steeply inclined to the volume axis, the cyclohexane line derived from the various sources mentioned has a gradient only one quarter as great. This anomaly is so very pronounced that petroleum technologists should find an early opportunity of investigating it. Meanwhile, there is a strong presumption that cyclohexane is not a predominant constituent in ordinary petrols. It may be remarked as a matter of some interest, that the expansion co-efficients deduced from Thorpe's values for the various members of the series, from C_6H_{12} to $C_{10}H_{20}$, show a big decline in the first three members, with approximate equality among the remainder. This is an example of the well-known anomolous tendencies in first members of series.

Dr. Barr had suggested the need for heating of the oils in contact with various metals and this had preoccupied the authors at an early stage of the work, but the difficulty of extending the experiments to even a few of the more typical bearing metals had then appeared too forbidding. The oil refiners would here find an interesting field for investigation, and presumably, from their more intimate knowledge of catalytic actions in oils, they would be able to make a judicious choice of the metals to be used.

As to Dr. Barr's very subtle observation on the tractions at the pegs of the Michell viscometer, no unreasonable anxiety need be encouraged. While it was clear that under certain conditions the pegs might exert an influence comparable with that of the main surface, the effect would be a viscosity effect, and thus the instrument would still remain a viscometer, which, subject to calibration, would yield useful results. It is clear, however, that in order to minimise such errors as might be introduced by the peg surfaces, and, of course, other errors, every effort should be made to attain uniformity in the manner and time of assembling the cup and ball.

Added Note.—Since the above was written the authors have found additional information in the "International Critical Tables," Vol. III. In Table I, on page 29, the values of the expansion co-efficients for cyclohexane are given, and these are embodied in the following equation:—

$$\rho_t = 0{\cdot}79707 - 0.8879\,t.\,10^{-3} - 0{\cdot}972\,t.^2 10^{-6} + 1{\cdot}55\,t.^3 10^{-9}$$

where ρ_t is the density at temperature t°C.

At 0°C. and 10°C. this equation gives values for the density equal to 0·79707 and 0·788095 respectively, compared with the

values from Thorpe utilised before, viz. 0·7598 and 0·7334 respectively. This reveals a discrepancy of 5 per cent. at 0°C. and 7¼ per cent at 10°C.

There is a strong presumption that the values in the "International Critical Tables" are more trustworthy than those given by Thorpe. For not only have they been independently verified in sources quoted in the "International Critical Tables," but the values bring the cyclohexane curve into Fig. 2 with remarkable agreement. It is unnecessary to make any alteration in Fig. 2, since it can be stated with considerable accuracy that the line for cyclohexane almost coincides with the line R which represents kerosine. Assuming that the "International Critical Tables'" values are correct, if would follow, not only that viscosity determinations have analytic value as between typical liquids, but further, that they provide an indirect check on density determinations.

The Composition of Petroleum (Kerosine and Other) Fractions.*

By J. A. Carpenter, M.A., A.I.C. (Member).

Part III.—Applications of the Aniline Point, Specific Gravity and Refractive Index Tests, with Properties of Individual Hydrocarbons.

In a previously published paper,[1] notes were given on the investigation of aromatics in Burmah and other spirit and kerosine fractions, together with a study of the application of the aniline point test to fractions boiling up to 300° C.

In the present part, amplifications and studies of further applications are given, together with some work on the identification and isolation of paraffins throughout the range, and of naphthenes in the lower range of fractions.

These studies are taken mainly through the use of the three principal tests mentioned above in combination with fractionating methods and it has been attempted to apply considerations similar to those of Ormandy and Craven[2] to the analysis of the constituents of various crude oils, particularly those from Burmah and Assam.

The main basis upon which these further studies rest is that of the isolation of, and determination of constants for, the whole range of paraffin hydrocarbons, followed by chemical and physical investigations on the nature of the naphthenes.

Such data (particularly regarding aniline points which provide the most convenient methods of all) can be applied to the study of the selective effect of solvents such as sulphur dioxide, sulphur dioxide-acetone mixture, phenol, aniline, etc., the nature of charging stocks and their cracked products, the value of different crudes from a refining point of view and the correct limits at which to cut finished products from them.

In fact, the development of the solvent phenol process[3] has depended for its checks entirely upon the application of aniline point methods, upon which the various partitions have been worked out.

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* Paper received May 1st, 1928.

[1] *Journ. Inst. Petr. Techn.*, 1926, **12**, 518.

[2] *Journ. Inst. Petr. Techn.*, 1924, **10**, 101.

[3] J. P. Fraser, Eng. Pat. 273,351 of 25.1.26 and 21.9.26.

The work has even yet only been developed incompletely owing to constant hindrance by local problems of a more immediately pressing nature, but even in its incomplete form, it demonstrates several points of interest.

The sections into which the work falls are as follows :—

1. The properties of aniline points.
2. Methods for the isolation of paraffins from fractions and, where possible, naphthenes and aromatics; partitions in aniline-oil systems.
3. (*a*) The examination of early fractions of Burmah crude and the identification of individual paraffins and naphthenes.
   (*b*) The examination of cracked Burmah wax.
4. Properties of paraffins (aniline points and other constants).
5. Properties of aromatics (aniline points and other constants).
6. Properties of naphthenes (aniline points and other constants).
7. Properties of unsaturateds (aniline points and other constants).
8. Correlation of the properties of 125–300° C. fractions from certain crudes (aniline points, specific gravity and refractive indices).
9. Rules for the determination of various classes of hydrocarbons in petroleum kerosine ranges.
10. General notes on the application of aniline point tests.

1. *The Properties of Aniline Points.*

The error introduced by the use of impure or wet aniline is too great to neglect.

Care must be taken also to avoid unnecessary or careless use of pipettes, for these may become sources of moisture.

Aniline must be redistilled carefully and if already contaminated by other hydrocarbons should be separated by solution in dilute hydrochloric acid, reliberated with alkali and redistilled with steam or after other extraction. The final constant boiling distillate should be dried by means of anyhdrous potassium carbonate and should be quite clear with nothing more than a very faint yellow tinge.

The experimental procedure for the miscibility, or "aniline point," test should be regulated according to the precautions already published in several papers and in the I.P.T. "Standard Methods of Testing Petroleum and its Products," whether used for spirits, kerosine fractions, wax or lubricants; even at the higher temperatures necessary for waxes, no error results if reasonable care is taken.

In general, aniline points of hydrocarbons :—

(1) Rise with molecular weight in the paraffin series.

(2) Rise with molecular weight with most simple types of naphthenes, but at lower values than those for corresponding paraffins.

(3) Remain in the region —20° C. to 0° C. for aromatic hydrocarbons.[4]

(4) Remain low for unsaturated hydrocarbons at values generally intermediate between those of aromatics and naphthenes, but vary considerably with the nature of the unsaturated body.[4]

(5) May rise as much as 20° C. with water saturated aniline, compared with dry freshly-distilled aniline.[1]

While the presence of aromatics and, to some extent, of naphthenes in hydrocarbon mixtures can be followed with fair accuracy through aniline point depressions, that of unsaturateds produces an effect which is too irregular to be followed accurately.[5]

The aniline point therefore must be an intimate function of the mutual solubility of the hydrocarbon and aniline as well as of that between the hydrocarbons themselves in the case of mixtures of hydrocarbons.[4]

The range of aniline points for paraffins boiling up to 300° C. at atmospheric pressure is approximately from 68° C. to 103° C., though higher up, the aniline point rises gradually to 154° C. for $C_{57}H_{116}$[1]; for naphthenes, the range is somewhat variable, but for the simple mononuclear type in the kerosine range, values are at least 20° C. lower than those of the corresponding paraffins.

2. *Methods for the Isolation of Paraffins, Naphthenes and Aromatics. Partitions in Aniline-oil Systems.*

The methods described below were indicated briefly in some cases in the author's previous paper[1]:—

(1) *Aromatics* were isolated for analytical and test purposes by Armstrong's method of acid treatment, which includes distillation of the aromatic sludge with superheated steam. This method destroys some and does not touch others, such as hexamethyl benzene, which does not sulphonate.

Another method for the isolation of impure aromatics lies in solvent extraction at low temperatures by aniline, phenol, and other solvents.

Brame and Hunter[4] comment on this and in their experiments obtained something less than a 40 per cent. concentration of aromatics in extracts in the range of spirits. The author has never isolated perfectly pure aromatics by this

[4] Brame and Hunter, *Journ. Inst. Petr. Techn.*, 1926, **13**, 794.
[5] Brame, *Journ. Inst. Petr. Techn.*, 1926, **12**, 48.

means ; he agrees with Brame and Hunter that by this method alone it is impossible to free hydrocarbon classes entirely from one another, owing to their mutual solubilities. However, the higher ranges yield comparatively pure aromatic extracts of the order of 75–80 per cent. purity in one extraction at low temperatures with the aid of water.

Subsequent redistillations and extractions improve this up to the order of 85 per cent. in the fractions under 300° C. For any determination depending on the use of such extracts given in the previous paper,[1] this was allowed for. Some partition values for a complete kerosine are given later, but a full discussion of this problem applied to narrow fractions must be left at present.

(2) *For paraffins* from $C_{20}H_{42}$ upwards to $C_{33}H_{68}$ and $C_{57}H_{116}$ usual refining methods were followed as far as the point at which moderately pure "high" and "low" melting point refined waxes of various grades could be obtained.

These were then severally distilled in vacuo or with very large quantities of steam, the resulting fractions being then recrystallised from benzol, petroleum spirit or ether by slow evaporation or fractional cooling.

Before purity could be obtained, it was found necessary to carry out as many as from eight to sixteen successive recrystallisations at this stage.

(3) *For paraffins* from $C_{13}H_{28}$ (B. Pt. 234° C/760 mm.) to $C_{19}H_{40}$ (B. Pt. 330° C./760 mm.) the methods employed were those of cutting to narrow limits by distillations (in vacuo or with steam for the higher members) after removal of aromatics. The resulting fractions were treated either by repeated fuming acid digestion, by strong nitration, by solvent extraction or by combinations of these methods (see below) and finally by freezing out the paraffins fractionally. For the higher members, ordinary ice cooling, for those boiling below 275° C. ($C_{15}H_{32}$ to $C_{13}H_{28}$) freezing mixtures of calcium chloride and ice were employed, and the frozen hydrocarbons were further fractionated by being gradually allowed to melt when allowed to warm up.

Good crystalline effects (in plates) were observed during these operations.

(4) *Lower paraffins* were prepared by means of similar methods, not including freezing ; the naphthenes present in their fractions were then removed by drastic sulphonation or nitration and refractionation.

(5) Pure high melting point paraffin hydrocarbons were cracked under 140 lbs. pressure in a bomb; the resulting pressure distillate was then treated as under (3) and (4) above.

In the cracking operation, large yields of pure paraffins were obtained moderately free from naphthenes, though they were accompanied by unsaturateds and aromatics. Sulphonation removed the aromatics, but appeared to produce naphthenes in limited quantity by the polymerisation of some of the unsaturateds (see detail under main sections 3 (*b*), 6 and 7).

(6) *Sulphonation Method.*—A volume of the aromatic-free fraction was shaken with oleum (20 per cent. SO_3) in a flask under a reflux condenser at 80° C.

Heating with occasional shaking was continued for seven or eight hours.

After settling in a separating funnel, losses were determined and the oil layer was washed with alkali after extraction with 10 per cent. of aqueous alcohol in the presence of a small pellet of sodium.

Finally the oil was dried with calcium chloride.

This method is mild and has to be repeated several times, but the advantage over more drastic methods rests in the fact that less paraffins are destroyed while all the naphthenes are eventually removed as aromatic sulphonic acids. Small quantities of ordinary aromatics can be recovered from the sludge by Armstrong's method.

(7) *Nitration Methods.*—One volume of aromatic free oil was nitrated with a well-cooled mixture of two volumes of fuming nitric acid and two volumes of fuming sulphuric acid in a large flask.

All was then agitated and warmed for eight hours at 60° C. (see note *) on a water bath.

The acid layer was separated and the intermediate layer of nitro bodies was then run off into a beaker of broken ice.

Dissolved nitro bodies were removed from the oil layer by reduction with tin and conc. HCl after which the resulting amino bodies were washed out with dilute HCl. The whole was warmed, treated with 98 per cent. sulphuric acid, alkali-washed and dried.

* Note.—In this method, the best temperature of treatment depends on the nature of the oil. With Badarpur fractions the reaction is apt to proceed with explosive violence, while with aromatic free Burmah and American fractions the reaction is more sluggish and can be carried out at 80° C. It is best to free the fraction partially by the milder sulphonation method and then carry out the strong nitration at as high a temperature as is found to be convenient, *i.e.* at which a brisk, but not explosive, evolution of nitrous fumes proceeds. It is a method in which a relatively high loss of paraffins is suffered.

(8) *Solvent extraction* in the liquid phase. The methods have been mentioned above in connection with the comments of Brame and Hunter.

In order to get the best out of them (say, by aniline) the fractionating effect of water on the aniline layer may be employed.

Aniline in various proportions is agitated at as low a temperature as convenient. The lower the temperature, the smaller is the volume of extract and the more concentrated in aromatics and naphthenes it becomes, while the net effect on the oil layer is much the same in each case.

If wet aniline is employed, the extract is smaller in volume and more concentrated in aromatics than if dry aniline is used ; similarly if a separated aniline layer is treated with water to saturation at the temperature of agitation, about half the extracted hydrocarbons are disengaged, forming an upper layer.

This upper layer is slightly richer in naphthenes but otherwise is not much different from the untreated oil, while the residual aniline layer contains a higher proportion of aromatics to total hydrocarbon than before. The addition of more and more water (up to saturation and formation of a third layer) gives an increasing concentration of aromatics in the liberated hydrocarbon layer, *i.e.* the first layer, liberated with small quantities of water, is rich in paraffins.

Thus, it is evident that the solubilities of the different classes of hydrocarbon in aniline are rendered more selective by the presence of water.

The aniline layer after water addition again divides into two layers on cooling, giving a high concentration of aromatics in the final aniline residue.

Such partitions are striking in the case of phenol (as seen in the development of the solvent phenol process[3]) owing to the greater solubility of water in phenol than in aniline.

The following tables 1–4 illustrate the kind of effect produced with untreated and aromatic free Burmah kerosines with aniline.

In the case of each oil, the two aniline points given refer to untreated oil and that treated with four volumes of 98 per cent. sulphuric acid respectively.

First Series.—Agitation of equal volumes of aniline and an untreated Burmah (150–280° C.) fraction of aniline pt. 54·6° C., aniline pt. after 98 per cent. H_2SO_4 72·0° C.

In each case:—

I. Dry aniline was used and the layers were separated. The aniline layer was then cooled to +10° C., 0° C., or —10° C. An upper hydrocarbon layer separated from a residual aniline layer, and both after separation were washed out with HCl, followed by water and finally dried with solid calcium chloride.

II. As in I. with removal of aniline layer. Water was added to this layer at the same temperature. After separating the two layers produced, the residual aniline layer was cooled as in I., and all three layers were then purified from aniline.

III. As in I., except that wet aniline, saturated with water, was used.

TABLE 1.

Agitation at 50° C. 100 c.c. oil + 100 c.c. aniline.

I. Dry aniline. Aniline layer 122 c.c. containing 41 c.c. of hydrocarbon.

	Oil septd. on cooling.			Oil from residue.		
	Volume c.c.	Aniline points ° C.	$N\frac{30}{D}$	Volume c.c.	Aniline points ° C.	$N\frac{30}{D}$
Cooled to 10° C.	28·6	59·2	1·445	12·4	5·4	1·490
		71·0	1·433		62·8	1·438
Cooled to 0° C.	29·2	58·4	1·446	11·8	0·6	1·495
		70·6	1·433		62·0	1·438
Cooled to —10° C.	30·0	58·0	1·446	11·0	—4·2	1·499
		70·5	1·434		61·8	1·439

II. Dry aniline, then water to saturation on aniline layer, then residue cooled. Original aniline layer 122 c.c. containing 41 c.c. hydrocarbon.

	Oil separated by water.			Oil separated on cooling.			Oil from final residue.		
	Vol.	An. Pts.	$N\frac{30}{D}$	Vol.	An. Pts.	$N\frac{30}{D}$	Vol.	An. Pts.	$N\frac{30}{D}$
Cooled to	21·0	60·0	1·445	7·0	56·8	1·451	13·0	7·0	1·494
+10° C.		72·2	1·434		69·0	1·436		63·0	1·440
Cooled to	21·0	60·0	1·446	7·4	56·2	1·451	12·5	3·0	1·498
0° C. ..		72·2	1·434		68·6	1·437		61·8	1·442
Cooled to	21·4	60·0	1·446	8·2	54·4	1·452	11·4	−2·0	1·505
−10° C.		72·2	1·434		68·0	1·437		61·6	1·442

III. Wet aniline. Aniline layer 108 c.c. with 19·5 c.c. hydrocarbon.

Cooled to				8·0	55·4	1·449	11·5	3·0	1·493
+10° C.					67·4	1·434		60·2	1·436
Cooled to				8·5	54·4	1·450	11·0	−3·6	1·498
0° C. ..					66·8	1·434		60·0	1·437
Cooled to				8·8	52·8	1·450	10·7	−8·2	1·502
−10° C.					66·2	1·434		59·2	1·438

TABLE 2. Agitation at 40° C.

I. Dry aniline. Aniline layer 108 c.c., containing 28 c.c. hydrocarbon.

Cooled to				13·0	58·6	1·446	14·8	7·2	1·490
+10° C.					70·6	1·434		63·0	1·440
Cooled to				15·8	57·0	1·447	12·2	−5·0	1·498
−10° C.					69·4	1·435		61·6	1·441

II. Dry aniline, then water to saturation on aniline layer, then residue cooled.

Cooled to	12·2	58·2	1·448	4·8	54·8	1·452	11·9	0	1·498
+10° C.		71·0	1·434		68·6	1·437		61·8	1·440
Cooled to	12·2	58·2	1·448	6·0	53·2	1·453	10·8	−9·0	1·501
−10° C.		71·0	1·434		67·2	1·437		60·0	1·442

III. Wet aniline. Aniline layer 110 c.c., containing 16·0 c.c. hydrocarbon.

Cooled to				5·0	57·2	1·453	11·0	0	1·493
+10° C.					69·2	1·435		61·4	1·437
Cooled to				5·6	56·6	1·458	10·4	−5·0	1·497
−10° C.					67·4	1·436		60·6	1·438

Similarly with agitations at lower temperatures, smaller volumes of extract result, *e.g.* at 30° C. dry aniline extracts 22·5 c.c. hydrocarbon, separating at 10° C. to layers containing 8·2 and 14·3 c.c.; at −10° C. to 10·2 and 12·3 c.c., while wet aniline similarly gives 3·2 and 11·4 at 10° C., 4·4 and 10·2 at −10° C., and so on.

Second Series.

TABLE 3.—Simple agitation of 100 c.c. untreated Burmah (150–275° C.) fraction with 100 c.c. dry aniline.

Aniline points of oil 54·6° C. and 71·2° C.

	Vol. aniline layer.	Vol. oil layer.	Volume oil A from aniline layer.	Volume oil B from oil layer.	An. Pts. Oil A ° C.	An. Pts. Oil B ° C.	An. Pt. Depression oil A ° C.	An. Pt. Depression oil B ° C.
—10° C. ..	106	94	11·0	89·0	–2	61·4	61·2	11·0
					59·2	72·4		
0° C. ..	108	92	13·0	87·0	5·4	61·2	55·0	11·0
					60·4	72·2		
15° C. ..	110	90	17·0	83·0	16·0	61·4	46·0	10·8
					62·0	72·2		
26·6° C.	113	87	21·0	79·0	26·0	61·6	38·0	11·0
					64·0	72·6		
40° C. ..	114	86	29·0	71·0	38·0	61·8	29·5	11·2
					67·5	73·0		
50° C. ..	120	80	40	60	45·3	61·6	24·1	11·4
					69·4	73·0		

Third Series.—Aromatic free Burmah fraction (150–280° C.).

Average boiling point 200° C., for which the aniline point of pure paraffin = 82° C.

Aniline point of fraction 72·0° C. (with approx. 50 per cent. naphthenes).

100 c.c. of above were agitated with 100 c.c. dry aniline at various temperatures.

TABLE 4.

Temperature of agitation.	Oil A from Aniline layer.	Oil B from Oil layer.	An. Pt. Oil A ° C.	An. Pt. Oil B ° C.	* Approx. Naphthenes in Oil A.
—10° C.	3·0	97·0	67·4	72·2	73
0° C.	3·6	96·4	68·0	72·1	70
15° C.	5·0	95·0	68·8	72·2	66
30° C.	7·6	92·4	69·4	72·2	63
40° C.	11·0	89·0	69·7	72·3	61·5
50° C.	15·0	85·0	70·1	72·3	59·5

The above series serve as rough illustrations of the partitions obtainable with a kerosine oil as a whole. In the first series there are a few apparent discrepancies in refractive index values, but the fraction is wide and the varying conditions of separation result in different allocations for individual naphthenes. Though R.I.'s were taken to five decimal places, no useful information is given beyond three.

* Calculated on the assumption that 1 per cent. naphthene depresses the aniline point by 0·2° C. The figures work out consistently on this basis.

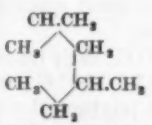
3(a). Early Fractions of Burmah Crude Oil.

It has been stated previously [1] that the hydrocarbons in Burmah oils show a tendency towards the presence of branching chain constituents, and that this general principle runs through the various classes of hydrocarbons, paraffins, aromatics and naphthenes alike.

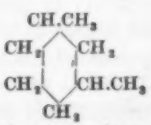
Some of the grounds on which this statement is based are seen below, but perhaps one thing that emerges is important in its bearing on the analytical work which follows.

Ormandy and Craven [2] and Egloff and Morrell [6] give curves for the specific gravity of naphthenes based on the simple ring prototypes, cyclohexane, cycloheptane, cyclooctane, etc., which possess far higher specific gravities than their smaller ring alkyl sidechain isomers. But there is very little evidence in favour of the presence of seven, eight, etc., rings, in fact, all the chemical and physical evidence obtainable points to the preponderance, in fractions below 220° C. at least, of cyclopentane and cyclohexane derivatives. The specific gravity curve for these is far less steep and not only is it more in agreement with observations for Burmah, Assam, Dutch East Indian, and certain American oils examined, but it represents the most probable type of naphthene, considering the accompanying aromatics. In higher fractions, and in Badarpur fractions especially, there is probably a proportion of condensed nuclear naphthenes based on a terpenic or naphthalenic structure as well as some members of the type of $\alpha\alpha$-dicyclo-hexyl ethane which contains two six-rings connected through an open side-chain. Large single rings deviate more and more from the stability expected from the strain theory; the definite presence of hexahydro toluene, -xylenes, -cumene, -mesitylene, etc., is deduced from the formation of well-defined nitro derivatives of the corresponding aromatics on nitration, though, as Brooks [7] remarks, rearrangements are apt to occur and it is not certain that a given aromatic derivative results from the correspondingly similar naphthene.

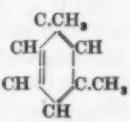
Still, the presence of such correlated bodies as the following are well indicated :—



A Dimethylhexane



A Dimethylcyclohexane



M-Xylene

[1] *Journ. Ind. Eng. Chem.*, 1926, **18**, 354.
[7] Non Benzenoid Hydrocarbons, pages 303/4

Fractionation.—The early fractions of Burmah crude oil were separated by dephlegmation, using eight section Young and Thomas columns, into 5° C. cuts. These were freed from aromatics and refractionated, one by one, several times. After four successive further fractionations into 2·5° C. cuts, each nominal range being collected from either fraction in its own receptacle and thus rearranged as fractionation proceeded, peaks appeared and grew more pronounced on repetition. The immediate neighbourhood of each peak was refractionated until the fractions showed very small variations from their professed values.

Final peak cuts, which represented the result of twelve successive operations, were then examined chemically and physically for separation of paraffins from naphthenes either by destruction of the latter, or by fractionation from aniline in combination with finishing treatments.

With very low fractions, true separation and conservation of the naphthenes could be effected, but for fractions at and above 100° C. this became increasingly difficult and in such cases it was necessary to deduce constants for the naphthenes from values to which the figures were approaching asymptotically or from values based on the found properties of the pure paraffin portion, together with the variations of proportions based on gravities or other properties as the naphthene was destroyed or partially extracted.

The peaks were constant boiling mixtures on which one aniline distillation[4] only made a small difference, while the volume of useful cuts became much too small on repetition several times. In some cases deductions were made from qualitative indications and known values, but this section is only intended as a qualitative study.

All specific gravities are given for $\frac{15{\cdot}5^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$

1. The hydrocarbon constituents of *natural gas* are CH_4, C_2H_6, C_3H_8 and some butane.

2. *Natural gasoline*, also scrubbings from cracked gas have been found qualitatively to contain *n*-butane (b.-pt. 1° C.). Isobutane $CH_3\ CH(CH_3)_2$ (b.-pt. —17° C.) is present in small quantities, together with pentanes and higher hydrocarbons.

3. Starting with *refinery crude* of I.B.P. 42–46° C., early fractions concentrate to a peak at 32–34° C. with sp. gr. 15·5/15·5° C.=0·627 to 0·635. Gravity and boiling points suggest a mixture of *n*-pentane and dimethyl ethyl methane.

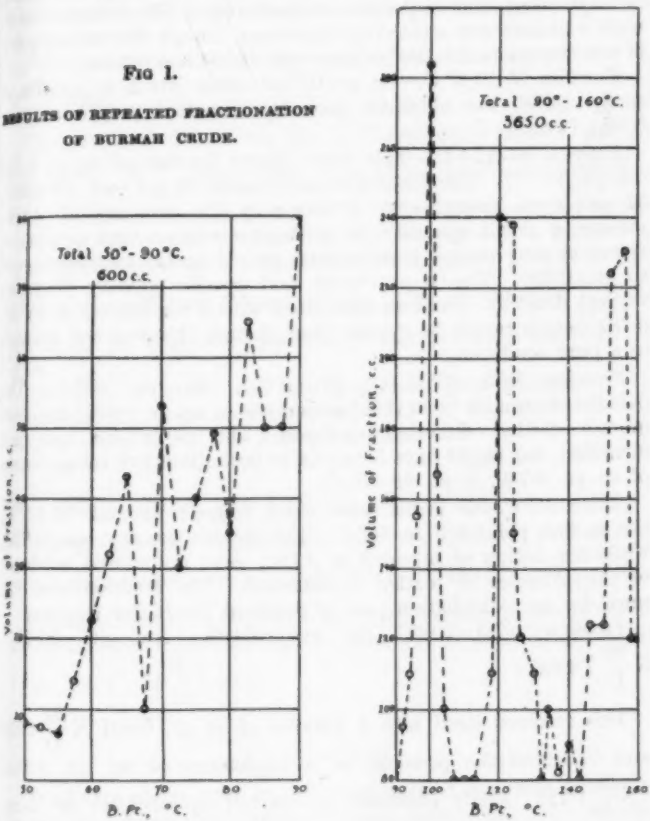
4. *From* 50°C. *to* 160° C. Fig. 1 shows the formation of peaks after refractionations of aromatic-free fractions at 62·5 – 65·0° C., 67·5 – 70·0° C., 75 – 77·5°C., 80·0 – 82·5° C., 87·5 – 90·0° C., 97·5 –

100° C., 117·5 – 120 – 122.5° C., 152·5 – 155° C., with minor peaks at 135° C. and 140° C.

Fraction 62·5 – 65·0° C.—Sp. gr. 0·6825. Very stable towards bromine in presence of $AlBr_3$; yields small quantities of acetic

FIG 1.

RESULTS OF REPEATED FRACTIONATION OF BURMAH CRUDE.



acid on prolonged oxidation with chromic acid. From gravity and boiling point it is probably methyl diethyl methane $CH_3\,CH(C_2H_5)_2$ or dimethyl propyl methane $(CH_3)_2\,CH\,C_3H_7$. No identification of di-isopropyl (b.-pt. 58° C.) or of trimethyl ethyl methane (b.-pt. 49° C.) could be obtained.

Fraction 67·5 – 70° C.—Sp. gr. 0·691. Aniline point 58·6° C. This was not acted on by bromine in the presence of $AlBr_3$, though fuming nitric acid acted upon it. Distillation with aniline gradually fractionated it into a hydrocarbon of sp. gr. 0·6645 (b.-pt. 70° C.) and another of sp. gr. 0·754 (b.-pt. 72° C.), the yields approximating to 70 per cent. and 30 per cent. respectively. The constants fit in with *n*-hexane and methyl cyclopentane, though the boiling point of the composite fraction is below the individual values.

Fraction 75–77·5° C.—Sp. gr. 0·7145, from which a paraffin of sp. gr. 0·6780 was obtained, probably trimethyl propyl methane $(CH_3)_3C.C_3H_7$.

Fraction 80–82·5 C.—This was a larger fraction of sp. gr. 0·724 (an. pt. 55° C.). Composed of approximately 63 per cent. paraffins, 37 per cent. naphthenes. Bromine in the presence of $AlBr_3$ yielded a small quantity of tri-bromo-benzene and prolonged nitration after aniline fractionation gave a stable hydrocarbon of sp. gr. 0·690. The b.-pt. range and specific gravity therefore suggest dimethyl pentanes associated with a naphthene of sp. gr. 0·781 (which would be cyclohexane, though this was not isolated in a pure condition).

Fraction 87·5 – 90° C.—Sp. gr. 0·725. An. pt. 55° C. The paraffin obtainable from this fraction was of sp. gr. 0·6975 and was impure diethyl - dimethyl - methane. The naphthene was not identified, but might have been one or both dimethylcyclopentanes of sp. gr. 0·759, b.-pt. 89–92° C.

Above 90° C. the yields were much larger; around 94–95° C. the aniline point fell to 54° C. The specific gravity was 0·735, while the action of bromine in $AlBr_3$ gave undoubted evidence of the presence of methyl cyclohexane. The fraction was not pure, for on redistillation part of it joined the higher fraction.

Fraction 97·5 – 100°C. Sp. gr. 0·7493. An. pt. 50·2° C. $N\frac{30}{D}$ 1·4066.

This resolved itself into a paraffin of sp. gr. 0·691 $N\frac{30}{D}$ 1·395 and indicated the presence of a naphthene of sp. gr. 0·7755 $\left(N\frac{30}{D}1{\cdot}419\right)$ easily identified as methyl cyclohexane or hexahydrotoluene through the formation of a penta bromo derivative.

These values give approximately 70 per cent. naphthene and 30 per cent. paraffin. The aniline point of the paraffin was 68°C., in which case each 1 per cent. naphthene depressed the aniline point by 0·25° C, a value slightly lower than that expected in this range.

The paraffin was almost certainly partly *n*-heptane, but the specific gravity and refractive index were high, values for *n*-heptane being 0·685 and 1·381. Another paraffin was therefore present and attempts to separate them met with little success. Presumably this other paraffin was trimethyl isobutyl methane, sp. gr. 0·695, b.-pt. 99·3° C, the octane used as an antiknock standard by some experimenters.[8]

Fraction 117·5–120° C. Sp. gr. 0·7502 An. pt. 59·6° C., $N\frac{30}{D}$ 1·4089.

The paraffins showed an. pt. 71° C., sp. gr. 0·717–0·721, b.-pt. 117–118° C., $N\frac{30}{D}$ 1·400. The naphthenes gave on nitration a trinitro derivative melting at 178–182°C., mostly trinitro *m*-xylene.

The paraffins were probably mostly composed of a mixture of dimethyl hexanes, for *n*-octane has a lower specific gravity (0·707), while the naphthenes (approximating to sp. gr. 0·776 $N\frac{30}{D}$ 1·420) contained 1·3 dimethyl cyclohexane and probably other derivatives.

Fractions at 135° C. *and* 140° C.—These gave evidence of the formation of trinitromesitylene m.p. 232° C., and trinitropseudocumene (m.p. 185° C.) on strong nitration.

Fraction 152·5–155° C. Sp. gr. 0·7763. An. pt. 63·2° C., $N\frac{30}{D}$ 1·4213. Sp. gr. paraffin 0·725. An. pt. 74° C.

The gravity was higher than that required for *n*-nonane (of which the constants are sp. gr. 0·7195, b.-pt. 149·5° C., $N\frac{30}{D}$ 1·401).

From the formation of trinitro isopropyl benzene (m.-pt. 107–9° C.) it was inferred that hexahydro cumene was present (sp. gr. 0·7946, b.-pt. 152°C., $N\frac{30}{D}$ 1·432).

General.

While the above work has not been carried out as an exhaustive study, strong evidence in favour of many definite side chain paraffins and cyclohexane derivatives exists.

As mentioned previously, it does not follow that naphthene hydrocarbons giving particular nitroderivatives are those of the expected structure, yet the probability still remains, while the

[8] Edgar, *Journ. Ind. Eng. Chem.*, 1926, **19**, 145.

constants deduced, or found, fit reasonably with expected values.

While undoubted variations in the aniline points of isomeric hydrocarbons low in the series exist as mentioned by Brame and Hunter[4], also Chavanne and Simon[9], yet the values obtained now for paraffins isolated from petroleum do not deviate more than slightly at any place from a general average curve based on boiling points or on numbers of carbon atoms in the molecule. The value given by Brame and Hunter for isodecane (diisoamyl) is very near the expected value for a boiling point of 173° C., though that of isopentane cannot be explained.

3 (*b*). *Cracked Burmah Wax.*—High melting-point wax, m.-pt. 58° C. was found to crack easily in a bomb of 140 lb. pressure, two hours under full pressure at a maximum temperature of 418° C. The resulting pressure distillate, which amounted to over 90·0 per cent. on the charge, was accompanied by no coke formation, but with the liberation of forty-eight volumes of gas.

When cut at 175° C. by dephlegmation for spirit and further distilled with steam for kerosine fractions, the spirit was found to contain 19 per cent. unsaturateds with 14·5 per cent. aromatics and the rest mostly paraffins with a small percentage of naphthenes. The kerosine had a far lower unsaturated content at about 3 per cent., with 12 per cent. aromatics.

After removal of unsaturateds and aromatics, fractions were cut at 5° C. intervals and pure paraffins were prepared from these by sulphonation, strong nitration and fractionation, those above 235° C. being finished off by freezing. The properties obtained are given in the next section. It was found that the aniline points were raised about 4° C. in each fraction by removal of naphthenes, though it is believed that many of these naphthenes resulted from the action of sulphuric acid on unsaturateds in the course of removal of the latter. (See page 468.)

On the eve of despatching this paper a note on the Analysis of Gas Oils and Hydrocarbon Oils from Tars by Griffith (*Jour. Soc. Chem. Ind.*, 1928, **47**, 21T) has just been received.

This experimenter obtained values for sulphonated hydrocarbons which apparently were not fully freed from bodies other than paraffins.

It has been found impossible to obtain purity of paraffins even with petroleum products, by the amount of treatment shown on page 23 (*loc cit*); furthermore, the values given for the specific gravities of paraffins recorded in literature were considerably higher than those given in most references. The aniline points in

[9] Comptes Rend, 1919, **168**, 1324.

Fig. 3 of Griffith's paper were considerably below those recorded here; this would follow from what has just been said regarding the non-purity of the paraffins. Furthermore, the "mean boiling point" should be deduced by averaging out narrow distillation fractional results, such as given in the A.S.T.M. method, on a proportional basis, rather than by taking the temperature at which half the distillate passed over. Further criticisms are provided by the numerical data which follow.

4. *Properties of Paraffins.*—The following table represents the properties obtained for the various members of the paraffin series from petroleum sources on a boiling point basis up to $C_{19}H_{40}$, thence on a melting-point basis without differentiation between normal and iso-paraffins, which in any case do not appear to deviate from values for synthetic paraffins in the higher ranges. All temperatures are in degrees centigrade.

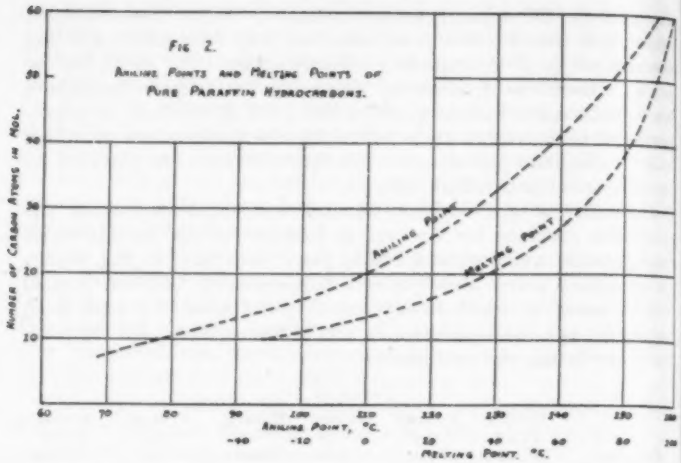
TABLE 5.

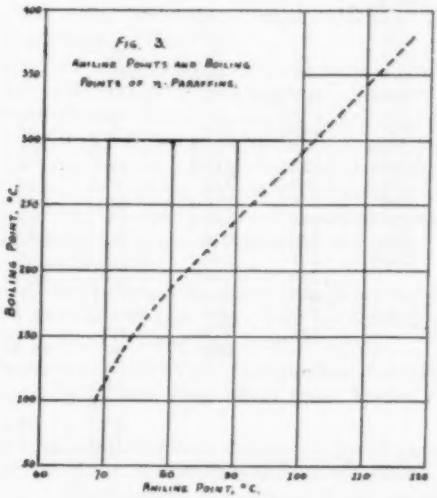
Paraffin	Boiling Point 760 mm. (of normal paraffin).	Boiling Point 50 mm.	Boiling Point 15 mm.	Melting Point (Theory)	Melting Point (obtained)	Aniline Point Values.
C_7H_{16} ..	98·4	27	4			68–69
C_8H_{18} ..	125·8	50	27			71–72
C_9H_{20} ..	149·5	70	45	—51		74
$C_{10}H_{22}$ ..	172	90	64·5	—32		77·5
$C_{11}H_{24}$ ..	194·5	108·5	82	—24		81·6
$C_{12}H_{26}$ ..	214·5	126	99	—12	Below —12	86
$C_{13}H_{28}$ ..	234	142·5	114	— 6	—8	89·5
$C_{14}H_{30}$ ..	252·5	158	129·5	+ 5·5	+4	93
$C_{15}H_{32}$ ..	270·5	173·5	143·5	10	8	96·5
$C_{16}H_{34}$ ..	287·5	187·5	158	19·5	19	99–100
$C_{17}H_{36}$ ..	303	201·5	170	23	23	103
$C_{18}H_{38}$ ..	317	215	181·5	28	28·2	105·8
$C_{19}H_{40}$ ..	330	226·5	193	32	32–33	108
$C_{20}H_{42}$ ..	(343)	237	205	37	37	110
$C_{21}H_{44}$ ..		256	224	44·4	44–45	114
$C_{24}H_{50}$ ..		275	239·5	51·1	51	118
$C_{25}H_{54}$ ..		293	255	56–57	56–57	121
$C_{28}H_{58}$ ..		311	274	62	62	124
$C_{30}H_{62}$ ..			289	66	66–67	126·8
$C_{36}H_{74}$ ..				70	70–71	129
$C_{40}H_{82}$ ..				81·5		138*
$C_{50}H_{102}$ ..				92·0		148*
$C_{77}H_{156}$ ..				96·5	96·5	154
$C_{80}H_{162}$ ..				99·5		156*

* Interpolated.

Curves for these values are given in Figs. 2 and 3.

The above aniline points are somewhat higher in some instances than those given in the previous paper, but they represent the highest values for narrow paraffin fractions, which have been obtained from various petroleum sources, including cracked P.D.





from wax, in later work. It has been possible to carry the purification further than previously, and the highest values for a given boiling-point will be the most correct.

Table 5, with Fig. 3, forms the basis for the aniline point determination of the various classes of hydrocarbons in kerosine fractions dealt with below (section 9).

Various physical properties, such as solubilities, expansions, densities and crystalline properties, have been determined for many of these hydrocarbons in continuation and revision of data pre-

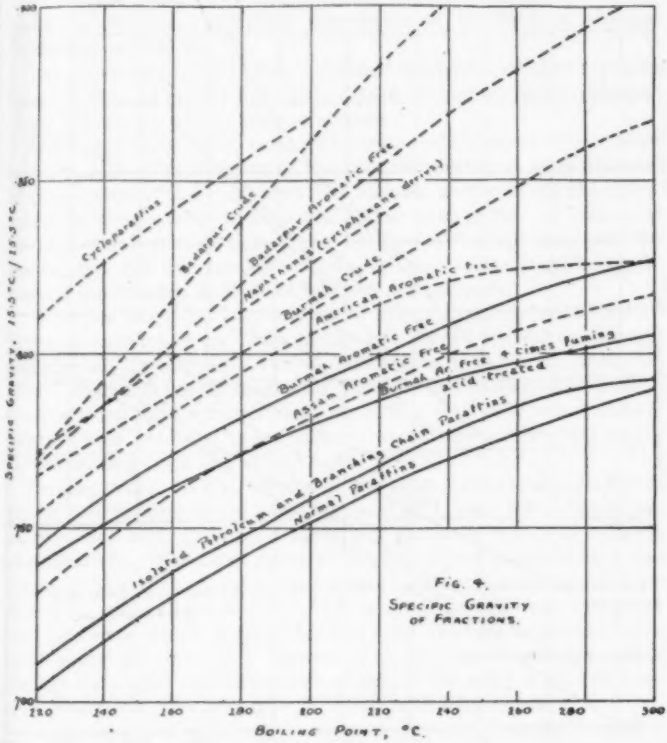


FIG. 4.
SPECIFIC GRAVITY OF FRACTIONS.

viously published by the author(10), but these will be considered at another time.

Specific gravities and refractive indices vary considerably between known isomers in the paraffin series, but when taken on a boiling-point or melting-point basis, lie along fairly regular curves

(10) *Journ. Inst. Petr. Tech.*, 1926, 12, 288.

which are given in Figs. 4 and 5. Certain values for synthetic normal paraffins as compiled from various sources lie along lower curves than those of the branching chain isomers; in all cases of paraffins isolated from petroleum fractions, with the exception of the lowest members in the spirit range, the values approximate to the branching-chain curve corrected for d $\frac{15{\cdot}5}{15{\cdot}5}$ and N $\frac{30}{D}$.

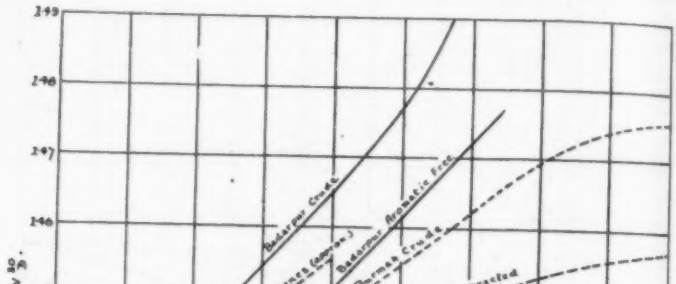


FIG. 5.
REFRACTIVE INDICES OF FRACTIONS.

(*Note.*—N $\frac{30}{D}$ was taken as the most convenient standard in Burmah, the decrease in R.I. per 1° C. being taken experimentally as 0·0004.)

5. *Properties of Aromatics.*—All the true aromatics so far studied have aniline points below 0° C. ranging down to —25° C., but as

obtained from petroleum have shown no regularity. Correlation of specific gravities and refractive indices also show irregularities; specific gravities vary from about 0·87 to over 1·0 according to structure, while refractive indices $\left(N\,\frac{30}{D}\right)$ likewise vary from 1·49 to over 1·55.

Unless the nature of the individual aromatics is known in any particular fraction, therefore, correlation of the various physical properties is difficult.

The previous paper[1] gives a detailed discussion of the aromatics found in certain crudes and their determination by aniline points; there is little to add to this at present.

Apart from miscibility tests with aniline, nitrobenzene[11] or other solvents, also determination of loss on acid treatment after removal of unsaturateds, there are very few reliable methods for the determination of aromatics in fractions higher than spirit. A refractive index method such as that given by Hoyte[12] is all very well for spirits, but not for ranges wherein the aromatics may be naphthalene derivatives as well as benzene homologues.

Attempts based on correlations of specific gravity or refractive index, as developed by Ormandy and Craven[2] for spirits, become complicated in kerosine ranges containing a mass of unknown mixed aromatics, naphthenes and paraffins and even with aromatic-free fractions appear from the curves in Fig. 5 to yield vague values. Again, there are very great differences between individual naphthenes boiling both above and below 220° C.

Further work on the effects of varying concentrations of sulphuric acid on petroleum fractions (see Fig. 1, page 550, of previous paper[1]) has been done on a variety of products with and without unsaturateds. The chief point of interest which arises is that the shape of the curve (aniline point-acid concentration) varies considerably with the nature of the aromatics. Solvent extracted fractions from which presumably the most reactive aromatics have been removed show flat curves at lower concentrations rising steeply for higher concentrations of acid; the same is true of low-spirit fractions, the aromatic in which is chiefly benzene.

The presence of other more easily sulphonated aromatics makes the curve rise quickly after a concentration of 85 per cent. acid.

Certain aromatics, such as hexamethyl benzene, depress the aniline point of a mixture, but do not react towards sulphuric acid; in such cases they will tend to be regarded as naphthenes of a particularly smoky type on burning a kerosine containing them. Such

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(11) Erskine, *Journ. Ind. Eng. Chem.*, 1926, **18**, 694, 722.
(12) Hoyte, *Journ. Inst. Petr. Tech.*, 1925, **11**, 76.

aromatics are probably the causes of discrepancies in the calculation of aromatics and naphthenes, which have often been found on separating classes of hydrocarbons by solvent extraction of fractions boiling over 250°.

6. *Properties of Naphthenes.*—This is one of the most difficult subjects in the study and one upon which considerably more work is needed as yet.

While it is comparatively easy to isolate pure paraffins and pure aromatics, even though the latter may have undergone drastic chemical changes in the process, it is not so easy to prepare pure naphthenes from petroleum, and the determination of aniline points of pure individual naphthenes up to the series remains yet to be done. In the lower ranges various isolations of relatively pure naphthenes were obtained by aniline fractionation at different times, but gave wide fluctuations of aniline points. Direct measurements of these and indirect observations higher up gave values approximating towards the following :—

From Fractions 80° C. to 90° C.	..	25° C. to 32° C. (Cyclohexane).
About 100° C.	..	40° C. to 41° C. (Methylcyclohexane).
About 120° C.	..	48° C. to 51° C. (Dimethylcyclohexane).
About 155° C.	..	53° C. to 56° C. (Hexahydro Cumene).
About 170° C.	..	57° C. to 59° C. (P-menthane).
About 200° C.	..	62° C. to 64° C. (Various).
About 250° C.	..	Fluctuating near 70° C.

On the other hand, Badarpur aromatic-free fractions gave lower aniline points than these, as follows :—

Fraction 200° C.	Aniline Pts.	58·5° C. (Pure Paraffin 82° C.)
225° C.		61·5° C. (Pure Paraffin 88° C.)
250° C.		65·2° C. (Paraffin 92·8° C.)
275° C.		69·0° C. (Paraffin 97° C.)
300° C.		73·0° C. (Paraffin 102·8° C.)

Hence naphthenes from ordinary Burmah, American and Assam sources in the kerosine range of fractions, appear to have aniline points some 20° C. below those of the pure paraffins of similar boiling point, while Badarpur fractions contain "naphthenes" with aniline points well over 20° C. below those of the pure paraffins and deviating further from the latter at higher temperatures. It is known that terpenes and partially hydrogenated naphthalenes depress aniline points by values intermediate between those for aromatics and simple naphthenes, also that Badarpur naphthenes give terpenic, camphoric and o-phthalic acid derivatives on oxidation, though they are not unsaturated bodies.

The effects of some types of condensed polynuclear naphthenes therefore appear to be greater than those of simple cyclohexane

derivatives,* while the higher naphthenes in Burmah and other crudes appear to follow nearer to the 20° C. depression of aniline point right up to 300° C. Until more definite and prolonged work has been done, more accurate values cannot be given and the values mentioned above are given with reserve, but the explanation of the Badarpur figures may also rest in the fact that amongst the increasingly high proportions of *aromatic* bodies present in the upper fractions, there is an increasing content of those which are not reactive to sulphuric acid, such as hexaalkyl benzenes, etc., which tend to depress the aniline points by more than would otherwise be expected.

It will be noted that the values of critical solution temperatures given by Chavanne and Simon[9] show variations between isomers of cyclohexane and cyclopentane derivatives, e.g. :—

Cyclohexane	31° C.
Methylcyclopentane	35° C.
Methylcyclohexane	41° C.
Dimethylcyclohexane	O—42·1° C.
	M—49·7° C.
	P—48·0° C.

and it is also deduced in their paper that the aniline constants of these acyclic hydrocarbons are independent of the size of the molecule, but differ considerably with structure.

The values now obtained by the author favour the depressions given by Ormandy and Craven[2] based on Tizard and Marshall's work in spirit ranges; in kerosine ranges the average value is deduced to be 0·2° C. per 1 per cent. naphthene, though at the higher limits near 300° C., the depressions given by certain complex polynuclear naphthenes may be greater, as they are in the spirit range.

In a note in comment on Kewley and Jackson's paper on the Burning of Mineral Oils in Wick-fed Lamps,[12] it was mentioned that the naphthenes in a Chindwin Valley crude were not unlike paraffins in their behaviour on burning, and that the structures of these compounds deduced from chemical experiments favoured the view that they were simple types of single-ring naphthenes with long open side chains. The aniline points of the naphthenes in these cases averaged 20° C. below those of pure paraffins, while the gravity and evidences of nitro-aromatics on nitration fitted in with observations on cyclohexane homologues.

7. *Properties of Unsaturateds.*—A few results obtained with wide fractions in the course of some independent cracking trials are given

* Note.—See discussion on Brame and Hunter's paper, pages 817 and 818. No confirmation of Craven's figure of 61° C. for mixed dimethyl cyclohexanes has been obtained.

[12] *Journ. Inst. Petr. Tech.*, 1927, **13**, 364 and 393.

simply in order to illustrate roughly the relations between aniline points and unsaturateds, but further detail has been avoided purposely.

The subject has not been treated as a separate study as yet, nor has it been taken to any depth, such as that given by Brame and Hunter.

The efficient estimation and removal of unsaturateds has not been settled completely in spite of the recent work of several experimenters ; for example, loss to 88 per cent. H_2SO_4 in a Babcock bottle cannot be exact owing to partial removal of aromatics, and it is by no means certain that all unsaturateds are removed by acid of less than 83–85 per cent. strength.

The higher (kerosine) fractions of pressure cracked distillates obtained contain much lower contents of unsaturateds than the spirit fractions, and a method similar to that used by Egloff and Morrell[4] for spirits has been found to give concordant results with pressure distillates derived from most charging stocks, though with certain sources more treatment is needed.

The method consists of treating with four volumes of 83 per cent. (by weight) sulphuric acid followed by distillation to the final boiling point originally obtained before treatment.

If the fraction still shows any appreciable colouration and aniline point depression with 83 per cent. acid, the process is repeated with 83 per cent. acid.

After allowing for all ordinary distillation losses, the dark polymerised residue above the F.B.P., together with treatment loss to acid are added to give the volume percentage of unsaturateds.

Egloff and Morrell used 80 per cent. acid, but it has been found that the second test nearly always shows the presence of small percentages of unsaturateds (0·4–0·6° C. A. Pt. differences), whereas four volumes of 83 per cent. acid seldom do unless the proportion of unsaturateds rises above 20 per cent. ; furthermore, there is no evidence of more than a very small loss of aromatics.

Eighty-eighty-five per cent. acid treatment, however, judging by the aniline points given in the following table, seems to give rise to the formation of small quantities of saturated naphthenes which appear in the final distillate (compare columns 4 and 8, Tables 7 (*a*) and 7 (*b*) which follow, and notice that the value in column 8 is lower than that in column 4).

Cracking of various charges was carried out in a bomb, fitted with a release valve, at 140 lbs. pressure, five hours under heat, two hours under full pressure at temperatures about 430° C.

Spirit fractions were cut at 175° C. and kerosine cuts were adjusted to an F.B.P. of 270° C.

TABLE 6.

TABLE 6.

The following table has been compiled from various sources (Landolt, Brooks, Day, Eisenlohr,[14] etc.) after correcting the densities to 15·5° C./15·5° C. and refractive indices to N_D^{30}.

Hydrocarbon.	B. Pt. ° C.	d. 15·5/15·5	N_D^{30}.
Cyclopentane	50·5	0·7555	1·402
Methyl-cyclopentane	72	0·7545	1·406
Cyclohexane	80·5	0·7825	1·423
1, 1, Dimethyl-cyclopentane	89	0·7465	1·409
1, 2, „ „	92	0·7577	1·409
Methyl-cyclohexane	100·5	0·7755	1·419
n-Propyl-cyclobutane	100	0·7485	1·408
Cycloheptane	117·5	0·8175	
1, 3, Dimethyl-cyclohexane	119+	0·7755	1·421
1, 1, „ „	120+	0·7850	1·426
1, 4, „ „	120+	0·7735	1·420
1, 2, „ „	123	0·7835	1·425
1 Methyl 2 Et. cyclopentane	121	0·7682	1·418
Ethyl-cyclohexane	130	0·7820	1·429
Propyl-cyclopentane	130	0·7763	1·421
Isopropyl „	128·5	0·7762	1·421
1, 1, 3 Trimethyl-cyclohexane	138	0·7945	1·432
1, 3, 5 „ „ (Mesityl)	138–140	0·7790	1·425
1, 2, 4 „ „ (Ps. cumene)	140/3	0·7895	1·425
1, 2, 3 „ „ (hemimell.)	145	0·7975	1·432
Cyclooctane	147·5	0·838	
1, 2 Me. Et. Cyclohexane	151	0·788	
Isopropyl „	152·5	0·7946	1·432
n-Propyl „	155	0·7910	1·432
Isobutyl „	157	0·808	1·440
1, 2, 4, 5 Tetramethyl	161	0·7895	1·430
1, 2, 3, 5 „	163	0·8185	1·442
Et. Cycloheptane	163	0·819	
Tert. Butyl cyclohexane	166	0·832	
Me. Isopropyl cyclohexanes (Cymene derivs.) :—			
Meta	166	0·803	
Para	169	0·808	
Ortho	171	0·818	
2 Cyclo hexyl— 2 Me. butane	191	0·824	
Di. Me. 1, 3, 5— Isobutyl cyclohex.	194	0·828	
1 Me. 2 isoamyl	204	0·814	
2 Cyclohex. 2 Me. pentane.	206	0·839	
Dekalin— (Decahydro naphthalene)	190	0·887	
Tetralin— (Tetrahydro naphthalene)	206	0·9815	
αα-dicyclo-hexyl ethane	256	0·9316	
Disuberyl	290	0·9145	

[14] *Journ. Inst. Petr. Techn.*, 1926, 12, 85A.

TABLE 7 (*a*).—Spirit Fractions.

Col. 1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	Nature of charge.
Cracking charge.	Aniline Points ° C. Untreated.	80% acid.	98% acid.	Loss to 80% acid.	Total unsats. by E. & M.'s method.	Aniline Points. Unsat.-free spirit. Finished.	98% acid.	Diffce. Cols. 2 & 7.	Average B. Pt. of spirit.	
1. Burmah 8% residuum from crude	51·4	54·4	67·8	7%	17%	56·0	66·8	4·6	120° C.	Paraffin-asphaltic mixed.
2. Ditto, another sample	52·2	56·0	67·6	6%	13%	56·4	67·0	4·2	120° C.	Ditto.
3. Sweats, heavy ends, Burmah	51·0	54·2	68·4	7%	15%	55·6	67·8	4·6	110° C.	Highly paraffinoid.
4. Heavy distillate cut, Burmah	50·4	54·0	67·6	6%	15%	54·6	66·8	4·2	120° C.	Paraffin-asphalt.
5. A topped Minbu crude	40·2	47·8	64·0	8%	26%	50·4	61·8	10·2	120° C.	Naphthenic.
6. A topped Masimpur crude	38·8	45·4	65·2	7%	25%	48·6	63·0	9·8	125° C.	Badarpur type of heavy naphthenes.
7. An Assam lubricant residue	47·0	53·6	69·2	7%	18%	55·2	68·4	8·2	120° C.	Mixed base.
8. An Assam crude 17% residuum	51·6	55·4	68·8	7%	14%	55·8	68·0	4·2	120° C.	Ditto.
9. A topped Palanyon crude	42·0		67·0	11%	23%	53·0	66·4	11·0	120° C.	Naphthenic type.
10. Burmah 58° C. M. Pt. wax	48·6	54·6	71·6	10%	19%	54·8	71·4	6·2	120° C.	Paraffin.

From the above table, the average aniline point depression per 1% unsaturated deduced from cols. 6 and 9 is 0·37° C., though the results are irregular. The distillation analyses of the finished products were practically the same as those of the originals.

TABLE 7 (*b*).—Kerosine Fractions.

1. Cracking charge. Number as above.	2. Aniline Points ° C. Untreated.	3. 80% acid.	4. 98% acid.	5. Loss to 80% acid.	6. Total unsat.	7. Aniline Points. Unsat.-free kero. Finished.	8. 98% acid.	9. Diff. cols. 2 & 7.	10. Average B. Pt. kerosine.
1	60	61	77·5	1%	3%	60·6	77·2	0·6	215° C.
2	60·4	60·6	78·2	1·5%	3%	61·0	76·0	0·6	220
3	66·2	66·4	80·0	1%	2%	66·6	79·0	0·4	220
4	59·2	59·4	77·0	1%	2%	59·4	76·4	0·2	220
5	35·0	36·0	67·0	2%	4%	37·0	66·8	2·0	210
6	12·0	12·4	68·6	2%	3%	12·4	69·2	0·4	220
7	56·2	56·6	76·4	1%	1·5%	56·4	75·6	0·2	210
8	61·4	61·8	79·4	2%	3%	62·0	79·2	0·6	220
9	45·4	46·2	70·2	—	3%	46·2	69·2	0·8	200
10	72·6	73·0	84·6	0·4%	1%	73·2	84·8	0·6	220

Average aniline point depression per 1% unsaturateds deduced from cols. 6 and 9, excluding charges No. 5 and 6, which are abnormal, is 0·157° C., but the differences of aniline points are too small for accuracy of application to such a study.

TABLE 9.—Specific Gravities at 15·5° C./15·5° C. See Fig. 4.

Description.	Fraction. 125° C.	150° C.	175° C.	200° C.	225° C.	250° C.	275° C.	300° C.
Normal Paraffins	0·7075	0·7230	0·7385	0·7510	0·7635	0·7725	0·7825	0·7900
Branching chain paraffins and petroleum paraffins	0·7150	0·7300	0·7460	0·7590	0·7710	0·7805	0·7900	0·7930
Simple naphthenes	0·7750	0·7925	0·8100	0·8260	0·8430			
(Dicyclic and polynuclear are much higher in higher fractions.)								
Unsaturateds	0·735	0·7625	0·780	0·7950				
(Compiled from other experimenters' publications.)								
Burmah crude	0·7680	0·7825	0·7965	0·8120	0·8275	0·8430	0·8570	0·8675
„ aromatic-free	0·7480	0·7650	0·7785	0·7910	0·8020	0·8120	0·8200	0·8275
„ after four fuming acid treatments or one strong nitration	0·7425	0·7575	0·7700	0·7780	0·7875	0·7930	0·8010	0·8050
„ purified paraffins	0·7150	0·7300	0·7460	0·7590	0·7710	0·7805	0·7900	0·7930
„ SO_2-acetone extracted (equal vols. at 30° C.)	0·7580	0·7725	0·7875	0·8000	0·8130	0·8245	0·8350	0·8430
Assam crude	0·7680	0·7850	0·8020	0·8160	0·8280	0·8425	0·8570	0·8680
„ aromatic-free	0·7350	0·7530	0·7700	0·7825	0·7950	0·8030	0·8110	0·8175
An American crude	0·7670	0·7850	0·8025	0·8170	0·8275	0·8365	0·8425	0·8470
„ aromatic-free	0·7580	0·7760	0·7925	0·8050	0·8160	0·8225	0·8250	0·8270
					0·8815	0·8880	0·910	0·9330

TABLE 7 (*a*).—Spirit Fractions.

Col. 1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	
Cracking charge.	Aniline Points ° C.			Loss to	Total unsats.	Aniline Points. Unsat.-free spirit.		Diffce. Cols.	Average B. Pt.	Nature of charge.
	Un-treated.	80% acid.	98% acid.	80% acid.	by E. & M.'s method.	Fin-ished.	98% acid.	2 & 7.	of spirit.	
1. Burmah 8% residuum from crude	51·4	54·4	67·8	7%	17%	56·0	66·8	4·6	120° C.	Paraffin-asphaltic mixed.
2. Ditto, another sample	52·2	56·0	67·6	6%	13%	56·4	67·0	4·2	120° C.	Ditto.
3. Sweats, heavy ends, Burmah ..	51·0	54·2	68·4	7%	15%	55·6	67·8	4·6	110° C.	Highly paraffinoid.
4. Heavy distillate cut, Burmah ..	50·4	54·0	67·6	6%	15%	54·6	66·8	4·2	120° C.	Paraffin-asphalt.
5. A topped Minbu crude	40·2	47·8	64·0	8%	26%	50·4	61·8	10·2	120° C.	Naphthenic.
6. A topped Masimpur crude ..	38·8	45·4	65·2	7%	25%	48·6	63·0	9·8	125° C.	Badarpur type of heavy naphthenes.
7. An Assam lubricant residue ..	47·0	53·6	69·2	7%	18%	55·2	68·4	8·2	120° C.	Mixed base.
8. An Assam crude 17% residuum	51·6	55·4	68·8	7%	14%	55·8	68·0	4·2	120° C.	Ditto.
9. A topped Palanyon crude ..	42·0		67·0	11%	23%	53·0	66·4	11·0	120° C.	Naphthenic type.
10. Burmah 58° C. M. Pt. wax ..	48·6	54·6	71·6	10%	19%	54·8	71·4	6·2	120° C.	Paraffin.

From the above table, the average aniline point depression per 1% unsaturated deduced from cols. 6 and 9 is 0·37° C., though the results are irregular. The distillation analyses of the finished products were practically the same as those of the originals.

TABLE 7 (*b*).—Kerosine Fractions.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Cracking charge.	Aniline Points ° C.			Loss to	Total	Aniline Points. Unsat.-free kero.		Diff. cols.	Average B. Pt.
Number as above.	Un-treated.	80% acid.	98% acid.	80% acid.	unsat.	Fin-ished.	98% acid.	2 & 7.	kerosine.
1	60	61	77·5	1%	3%	60·6	77·2	0·6	215° C.
2	60·4	60·6	78·2	1·5%	3%	61·0	76·0	0·6	220
3	66·2	66·4	80·0	1%	2%	66·6	79·0	0·4	220
4	59·2	59·4	77·0	1%	2%	59·4	76·4	0·2	220
5	35·0	36·0	67·0	2%	4%	37·0	66·8	2·0	210
6	12·0	12·4	68·6	2%	3%	12·4	69·2	0·4	220
7	56·2	56·6	76·4	1%	1·5%	56·4	75·6	0·2	210
8	61·4	61·8	79·4	2%	3%	62·0	79·2	0·6	220
9	45·4	46·2	70·2	—	3%	46·2	69·2	0·8	200
10	72·6	73·0	84·6	0·4%	1%	73·2	84·8	0·6	220

Average aniline point depression per 1% unsaturateds deduced from cols. 6 and 9, excluding charges No. 5 and 6, which are abnormal, is 0·157° C., but the differences of aniline points are too small for accuracy of application to such a study.

TABLE 9.—Specific Gravities at 15·5° C./15·5° C. See Fig. 4.

10	72·6	73·0	84·6	0·4%	1%	73·2	84·8	0·6	220

Average aniline point depression per 1% unsaturateds deduced from cols. 6 and 9, excluding charges No. 5 and 6, which are abnormal, is 0·157° C., but the differences of aniline points are too small for accuracy of application to such a study.

TABLE 9.—Specific Gravities at 15·5° C./15·5° C. See Fig. 4.

Description.	Fraction. 125° C.	150° C.	175° C.	200° C.	225° C.	250° C.	275° C.	300° C.
Normal Paraffins	0·7075	0·7230	0·7385	0·7510	0·7635	0·7725	0·7825	0·7900
Branching chain paraffins and petroleum paraffins	0·7150	0·7300	0·7460	0·7590	0·7710	0·7805	0·7900	0·7930
Simple naphthenes	0·7750	0·7925	0·8100	0·8260	0·8430			
(Dicyclic and polynuclear are much higher in higher fractions.)								
Unsaturateds	0·735	0·7625	0·780	0·7950				
(Compiled from other experimenters' publications.)								
Burmah crude	0·7680	0·7825	0·7965	0·8120	0·8275	0·8430	0·8570	0·8675
,, aromatic-free	0·7480	0·7650	0·7785	0·7910	0·8020	0·8120	0·8200	0·8275
,, after four fuming acid treatments or one strong nitration	0·7425	0·7575	0·7700	0·7780	0·7875	0·7930	0·8010	0·8050
,, purified paraffins	0·7150	0·7300	0·7460	0·7590	0·7710	0·7805	0·7900	0·7930
,, SO_2-acetone extracted (equal vols. at 30° C.)	0·7580	0·7725	0·7875	0·8000	0·8130	0·8245	0·8350	0·8430
Assam crude	0·7680	0·7850	0·8020	0·8160	0·8280	0·8425	0·8570	0·8680
,, aromatic-free	0·7350	0·7530	0·7700	0·7825	0·7950	0·8030	0·8110	0·8175
An American crude	0·7670	0·7850	0·8025	0·8170	0·8275	0·8365	0·8425	0·8470
,, aromatic-free	0·7580	0·7760	0·7925	0·8050	0·8160	0·8225	0·8250	0·8270
Badarpur crude	0·7755	0·8050	0·8325	0·8615	0·8880	0·910	0·9330	—
,, aromatic-free	0·7725	0·7940	0·8155	0·8380	0·8575	0·8760	0·8915	0·9050

TABLE 10.—Average Refractive Indices for D Line at 30° C. See Fig. 5.

Description.	Fraction. 125° C.	150° C.	175° C.	200° C.	225° C.	250° C.	275° C.	300° C.
Normal paraffins	1·392	1·400	1·408	1·417	1·425	1·433	1·439	1·442
Branching chain and petroleum paraffins	1·397	1·4035	1·4115	1·419	1·4265	1·435	1·440	1·4425
Simple naphthenes	1·420/5	1·433/ 1·440	1·445, etc.					
(These fluctuate very widely.)								
Burmah crude	1·423	1·431	1·439	1·447	1·4565	1·466	1·4735	1·4755
,, aromatic-free	1·4125	1·419	1·425	1·431	1·437	1·442	1·445	1·446
,, after four fuming acid treatments	1·407	1·413	1·420	1·4265	1·433	1·438	1·442	1·445
,, purified paraffins	As above.							
,, SO_2-acetone extracted (equal vols. at 30° C.)	1·4195	1·426	1·433	1·440	1·446	1·4515	1·455	1·457
Badarpur crude	—	1·438	1·451	1·465	1·481	Rises rapidly.		
,, aromatic-free	—	1·4275	1·439	1·4505	1·464	1·477		

TABLE 11.—Aniline Points. See Fig. 6.

All in degrees centigrade.

Description.	Fraction. 125° C.	150° C.	175° C.	200° C.	225° C.	250° C.	275° C.	300° C.
Paraffins	71·3	74·2	78·0	82·8	87·9	92·6	97·2	102·3
Simple naphthenes	Approximately 20 °C. below above ; see notes, page 466.							
Burmah crude	43·0	46·0	51·5	56·0	59·5	62·4	64·7	66·5
,, aromatic-free	59·0	64·2	68·6	71·8	75·0	80·5	86·2	91·5
,, after four fuming acid treatments	63·0	67·0	71·5	75·0	79·5	85·2	90·2	96·5
,, SO_2-acetone extracted	54·0	56·0	59·5	64·6	69·4	73·2	76·3	79·0
Assam crude	35·0	36·5	43·0	50·3	58·2	60·9	63·0	66·0
,, aromatic-free	61·5	65·4	69·8	73·3	78·0	83·0	88·0	94·5
An American crude	50·0	52·0	54·0	57·5	62·5	67·9	71·3	75·0
,, aromatic-free	55·0	57·8	61·0	66·0	72·0	78·0	82·5	87·0
Badarpur crude	49·0	43·0	39·0	34·0	32·0	27·0	18·8	9·8
,, aromatic-free	55·5	55·7	57·0	58·5	61·5	65·2	69·0	72·5

Ordinary refining was carried out before the aniline points were taken, either by acid treatment of P.D. followed by distillation into cuts and a finishing bauxite filtration, or by distillation of untreated P.D. into cuts, followed by acid treatment, washing and

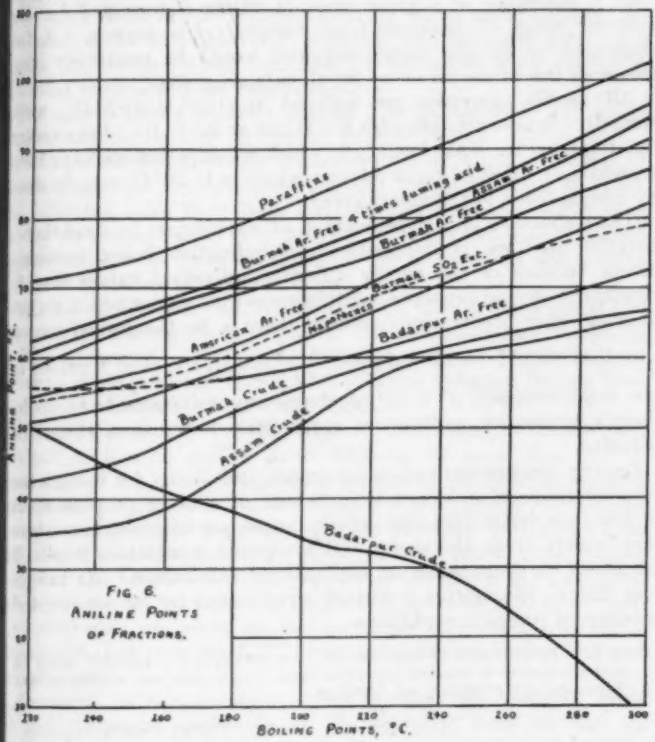


FIG. 6.
ANILINE POINTS OF FRACTIONS.

redistillation of the cuts which were then finished with a bauxite filtration.

The table below gives values for 80 per cent. acid with which the series of trials was carried out; the full effect of 83 per cent. acid may be taken as giving slightly higher values for columns 3, 5, 6 and 7 than those actually in this table for spirits.

The effect due to the reduction of nearly all the unsaturated content is, however, sufficiently reflected in the table and the net ratio between columns 6 and 9 is very little affected. In view of

the irregularity of the results, it has not been considered worth while to carry these points further.

8. *Properties of* 125–300° *C. Fractions from Certain Crude Sources.* (Specific gravity, refractive index, aniline point.)—Figures 4, 5 and 6, together with the following Tables 9–12, give in condensed form a summary of a great mass of values determined for the kerosine range of fractions from various crude sources. A full statement of all the values obtained would be needlessly long, therefore the values for every 25° C. only are given.

All specific gravities are reduced to 15·5° C./15·5° C., while refractive indices are taken for the D line at 30° C. (i.e., the average day temperature of the locality in which the experiments have been carried out). Reduction of refractive indices to 20° C. may be done by adding 0·004 to the values given.

The deduction of the percentage of naphthenes in naphthene-paraffin mixtures is impossible from refractive index measurements because of the widely differing individual values due to structure. Actual proportional differences give values which do not fit with other observations—indeed there is no theoretical reason why they should—while values of $\frac{n-1}{d}$ are all too close together in the neighbourhood of 0·550 to enable any deductions to be made, though values for naphthenes are a little lower than those for paraffins.

Gravity measurements give inaccurate indications, for though the preponderance of evidence is in favour of a large proportion of cyclohexane derivatives over certain ranges, yet individual members vary widely from the mean and erroneous conclusions result if the mean curve is taken as the basis of calculation. At ranges over 220° C. the matter is further complicated by the undoubted presence of complex naphthenes.

TABLE 12. Percentages of naphthenes in aromatic-free fractions based on proportionality of specific gravities, refractive indices and aniline points.

Fraction.	125° C. 150° C.	175° C.	200° C.	225° C.
I. From specific gravities, ref. Table 9.				
(*a*) Burmah Aromatic-free	55	56	51	48	43
(*b*) Assam ,,	35	37	37	35	33
(*c*) American ,,	72	74	73	69	63
II. From refractive index proportionality directly, ref. Table 10.					
(*a*) Burmah Aromatic-free (Same oil as I. (*a*).)	61	50	41		
III. From aniline points. Ref. Table 11.					
(*a*) Burmah Aromatic-free	61	50	47	55	64
(*b*) Assam ,,	49	44	41	47	49
(*c*) American ,, (Same oils as in I.)	81	82	85	84	79

On the whole, the aniline point values give what may be regarded as the nearest probable approaches to accuracy, and indeed a very large number of deductions based on the rules given below fit in quite well with interlocking observations and summation values deduced from narrow and wide cuts under solvent extraction. Even here there are no accurate data on which exact reliance can be placed, and some crudes (*e.g.*, Badarpur and Miri) give anomalous results, in which certain non-reactive aromatics may easily be classified erroneously as naphthenes.

The above tables at least suggest the impossibility of basing determinations directly on specific gravity values.

9. *Tentative Rules for the Determination of Various Classes of Hydrocarbons in Kerosines.*—From the foregoing considerations, the following rules have been deduced and applied. While they are by no means exact, they provide results which give sufficient approximations to be of considerable use in assessing the relative values of kerosines of different types.

The kerosine is analysed by the A.S.T.M. distillation method and the average boiling point deduced. Aniline points are taken for (*a*) the untreated oil, (*b*) after agitation for one hour with four volumes of 83 per cent. H_2SO_4, and (*c*) after agitation for one hour with four volumes of 98 per cent. H_2SO_4.

If the 83 per cent. acid treatment after alkali wash yields a coloured product or has an aniline point differing by more than 0·2° C. from that of the untreated product (as will be the case for cracked kerosines), it is redistilled to the original F.B.P., noting the distillation percentages. If the retest with 83 per cent. acid shows that sufficient treatment has been given (if not, repeat), the aniline points of the product redistilled as far as the first F.B.P. are then taken (*d*) after 83 per cent. and (*e*) after 98 per cent. acid treatment.

Unsaturateds are given by loss to 83 per cent. acid treatment, plus residue left over the F.B.P. (correcting for distillation loss and recondensate).

Aromatics in the unsaturated-free portion are deduced from (*b*) and (*c*) where applicable, or, if necessary, from (*d*) and (*e*) according to the method given in the previous paper.

Naphthenes in the aromatic-free portion, (*c*) or (*e*), whichever is applicable, are deduced on the assumption that every 5 per cent. naphthene depresses the aniline point by 1° C. from the A. Pt. given by pure paraffins of the same average boiling point (which can be deduced from the final distillation analysis).

Paraffins in (*c*) or (*e*) are deduced by difference.

It will be noted from the aniline point values for paraffins, that considerable corrections are necessary to values deduced from Egloff and Morrell's (⁸) method for unsaturateds in spirits with high

F.B.P.'s, such as American Navy end point gasoline. This point and certain others noted above are touched on by Ford[15] in work on transformer coils.

As an example, suppose the data collected are as follows :—

Loss to 83% acid .. ..= 8%
Residue over F.B.P. (corrected) .. ..=12%
Average B. Pt. fraction after redistillation .. ..=215° C.
(For which A. Pt. of pure paraffin is .. .. .. 86° C.
See Table 5, page 461, and Figs. 3 and 6.)
An. Pt. (*d*) after 83% acid .. ..= 61·8° C.
(*e*) after 98% acid .. ..= 80° C.
Unsaturateds = 8 + 12 .. ..=20% on original (by vol.)
Aromatics = 20% of the 80% unsat.-free .. ..=16% on original (by vol.)
(Depression = 18·2° C., corresponding to 20% by volume aromatics, see Table XX., page 564, previous paper (1) and extracted below for convenience.)
Aromatic-free residue = 100—36.. .. .. ..=64%
Naphthenes = (86—80) × 5 = 30% of the 64% ar.-free=19·2% on original
Paraffins = 64—19·2 .. ..=44·8% on original

TABLE 13.

Extracts from Table XX. in previous paper, reproduced for convenience. (Applicable to fractions between 125–300° C. in which the aromatic-free portion contains at least 30 per cent. paraffins and no unsaturateds.)

% Aromatics. By vol.	% Aromatics. By weight.	An. Pt. Depression. ° C.	% Aromatics. By vol.	% Aromatics. By weight.	An. Pt. Depression. ° C.
1	1·15	0·8	18	20·0	16·2
2	2·3	1·6	20	22·1	18·2
4	4·5	3·4	22	24·3	20·2
5	5·6	4·2	24	26·4	22·1
8	9·0	7·0	26	28·5	24·0
10	11·2	8·8	30	32·7	27·8
12	13·4	10·6	36	39·0	33·7
14	15·6	12·5	40	43·1	38·0
16	17·8	14·3			

N.B.—The higher values should be avoided by means of dilution with a known volume of the same aromatic-free fraction and calculation by proportion.

It is possible that considerable criticism will be directed against the above as being of such an approximate nature only. This is fully realised in conjunction with the fact that so much work yet remains to be done on the subject, and in view of the various criticisms of such methods expressed in the discussion on Brame and Hunter's paper which was only received after the work detailed in the present paper had been carried out and compiled. The only work done since that paper and discussion have been received, consists of a few further attempts at aniline fractionation of paraffin-naphthene mixtures and their incorporation with remarks in these

[15] *Journ. Ind. Eng. Chem.*, 1927, **19**, 1165.

notes. Attempts to apply the Gladstone and Dale, also the Lorenz-Lorentz, specific refraction applications of Ormandy and Craven to aromatic-free kerosine fractions containing mixed types of all kinds of naphthenes and paraffins have not met with success though their application to known binary mixtures is another matter. Refractive indices have been determined to more decimal places than given above, but this accuracy is wasted in view of the diversity of the unknown hydrocarbons. While aniline points suffer from this defect in some measure, it yet seems surprising, in view of their wide application, that so little work has been published on them and that so many misquotations still occur in literature and comments on them. The possibilities of the aniline point method, however, seem to be greater than may be supposed from a perusal of the criticisms to which reference has been made above, and in which the method is dismissed as being unreliable.

Locally the study of kerosines is of more vital interest than that of spirits and whatever may be said about the supposed drawbacks of the methods, not only have they been of the utmost value in working out several problems connected with kerosines, but they have been applied with success in actual large-scale practice, certainly with regard to the determination of aromatics and in a general measure with regard to the approximate estimation of naphthenes, both of which bear on the assessment of the refining potentialities and burning qualities of kerosines.

10. *General Notes on the Application of Aniline Point Tests.*—There are many everyday problems connected with the properties of petroleum fractions upon which immediate information is given by the values of aniline points.

The following indicate a few examples :—

(1) Many kerosines give low aniline points after treatment with four volumes of 98 per cent. H_2SO_4.

Depending on the depression of A. Pt. due to aromatics, it is found that such kerosines usually burn indifferently, the aromatic-free portion being highly naphthenic and deficient in paraffins.

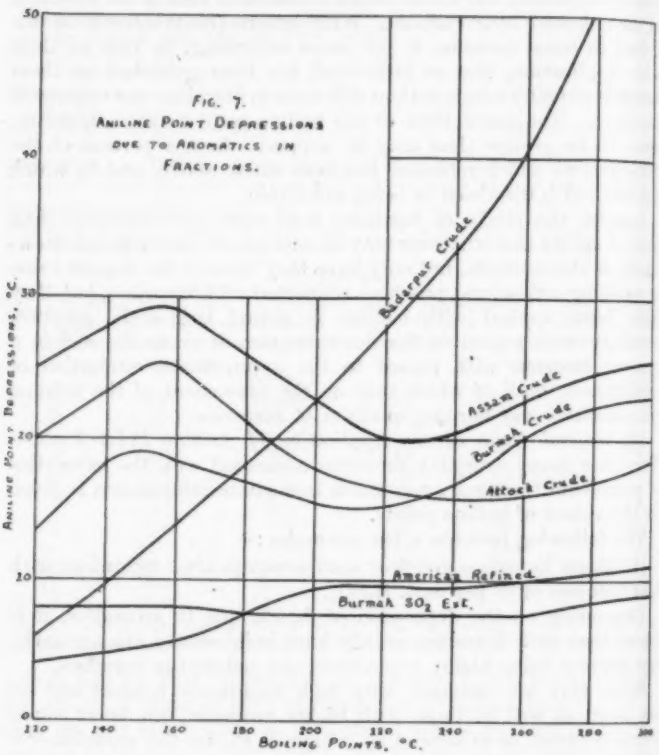
Some give low aromatic with high naphthenic content and do not burn as well as those with higher aromatic, yet lower naphthenic content, as evidenced by a high A. Pt. for the aromatic-free portion.

The test shows difference in the sources from which the kerosines are drawn and is valuable from this point of view for identification purposes.

(2) The same considerations show rapidly whether the fractions of a crude corresponding to kerosine are likely to be profitably improved by solvent extraction methods, such as SO_2 or phenol treatments.

In some cases, such as Badarpur fractions, it will not be advantageous to remove aromatics, because the residual naphthenes themselves will not burn reasonably.

Again, aromatics may be in too great a proportion to yield an adequate return after losses are substracted unless these aromatics can be profitably employed in admixture with spirit fractions.



(3) On cracking different kinds of charging stocks, the test shows how the resulting cuts from the pressure distillate are likely to behave, and in general demonstrate how the nature of the cracked products is governed by the nature of the charging stock.

(4) Curves in Fig. 7 show from aniline point depressions how aromatics are distributed or become formed on distillation.

Thus, it is seen from the curves and it is verified in practice that:—

(*a*) An Assam kerosine is best cut to avoid spirits fractions as well as heavy ends.

Hence the refining treatment of Assam crude should be both that of producing maximum spirit and of keeping the F.B.P. of the kerosine reasonably low. The increase of aromatic content at the light end of the kerosine tends to offset any advantage due to the inclusion of lighter boiling fractions through lower viscosity and surface tension effects (see Kewley and Jackson's paper [13]).

(*b*) With Badarpur, on the other hand, where sufficiently light fractions exist at all in the crude oil from any well, kerosines must be cut as low as possible owing to the enormous increase in aromatic content as the range goes up. Even when the aromatics are partially or completely removed, however, Fig. 6 shows that naphthene contents are high and they are found to be poor from a burning point of view.

(*c*) Solvent extracted kerosines and those from certain paraffin crudes exhibit a more even curve, so that it does not matter from the aromatic point of view where they are cut, and this matter can be regulated entirely from other considerations. The effect of such aromatic-removing solvents is to flatten the curve, while the A. Pts. after acid treatment furnish information regarding the residual hydrocarbons.

Summary.

1. Aniline point determinations throughout the boiling point ranges of kerosine oil are determined for paraffins and other classes of hydrocarbons, and for paraffins in the solid wax range.

2. Paraffins have been isolated throughout the whole series, while naphthenes have shown greater difficulty.

In general, all other classes of hydrocarbons can be removed chemically by sulphonation, nitration or solvent extraction combined with the above methods.

In the higher ranges, these methods are supplemented by freezing.

3. Early fractions of Burmah crudes contain high proportions of branching chain paraffins, also naphthenes based on cyclopentane and cyclohexane rings. There is no evidence that large rings exist in petroleum naphthenes in these crudes, though their presence has been assumed in various petroleum fractions by certain other workers.

4. Simple types of naphthenes have aniline points about 20° C. below those of their paraffin counterparts, while the effect of

unsaturateds is very irregular. In some cases, the determination of naphthenes is possibly affected by the presence of aromatics which are not acted on by sulphuric acid or by certain polynuclear substances which possess low aniline points.

5. Attempts to correlate specific gravities and refractive indices with a view to the determination of the different classes of hydrocarbons are upset by great variations in the values for individual members.

6. Tentative rules for the determination of unsaturateds, aromatics, naphthenes and paraffins, based on aniline point determinations in conjunction with acid treatments, are given for kerosine fractions.

7. Applications of the aniline point method are particularly suitable in such problems as identification of kerosines from different sources, forecast of their burning qualities, determinations required on working out the effect of solvent extractors, decision as to best points at which to cut refined products, determinations of the nature of cracked products and the value of various crudes from a refining point of view.

In conclusion, the author acknowledges the assistance of Maung Maung, B.Sc., A.R.C.S., Mr. A. Sirker, M.Sc., and Mg Hla Oung, and wishes to thank the Directors of the Burmah Oil Company for kind permission to publish the work, also Mr. W. J. Wilson, A.C.G.I., F.I.C., for kind assistance in correcting proofs.

The Examination of Petroleum Distillates from Various Sources.*

Part I.—The Preparation of a Standard Motor Spirit and a Standard Kerosine.

By S. T. Minchin, B.Sc., A.I.C. (Assoc. Member) and G. R. Nixon, A.R.C.Sc., B.Sc.

Of late it has been the tendency of chemists in the petroleum industry to classify the chief constituents of motor spirit and kerosine as follows :— (*a*) Unsaturated hydrocarbons, (*b*) Aromatic hydrocarbons, (*c*) Naphthene hydrocarbons, and (*d*) Paraffin hydrocarbons.

At present it is not possible to define rigidly each class, since hydrocarbons are known which possess the properties of more than one class, *e.g.* cyclohexene is an unsaturated naphthene, while propylbenzene is an aromatic hydrocarbon with a paraffin side chain. Class (*c*) is the most ill-defined, because of the lack of systematic knowledge of these hydrocarbons; to avoid confusion in this work we will consider as belonging to this class (*i*) cyclobutane, cyclopentane, cyclohexane, cycloheptane and their alkyl derivatives, (*ii*) decahydronaphthalene and related compounds.

A motor spirit is of excellent quality if rich in aromatics (preferably toluene), naphthenes, certain kinds of unsaturates; paraffins being the least useful class apart from volatility. On the other hand a kerosine with a high paraffin content is vastly superior to one containing aromatics and naphthenes from the point of view of illuminating value.

In a good lubricating oil the tendency for specifications to include low specific gravity and wax content, with high viscosity and flash point indicates the desirability of naphthenes. Here, however, the importance of type must be emphasised, since, as will be shown in a later part of this series, it is possible to have a purely naphthenic oil of relatively high specific gravity and low viscosity.

It is evident that although for simplicity it is generally assumed that these classes are distinct, actually they merge into one another, and this tendency is more noticeable with increasing molecular weight.

To isolate completely any given class is extremely difficult, and to separate the individual members of a class is well nigh impossible,

* Paper received May 1st, 1928.

though Mabery claims to have obtained individual naphthenes from Pennsylvanian lubricating oil. However, the structure of such compounds and the isolation of many more have to be established before the work can be of use in relation to the general problem of the composition of petroleum.

On the other hand, as the use of the various fractions becomes more defined, and therefore more rigorously specified, so does the necessity for accurate testing and scientific refining become more acute.

The position is such that the investigator is forced for the present to deal with properties peculiar to each class, and as the use of chemical reagents cannot be considered as a distinctive method of discriminating between the hydrocarbons present, such properties are preferably physical properties.

From time to time various methods have been proposed and used to estimate the extent to which these classes are represented in motor spirit and kerosine from various sources, and the effect each class has on the quality of these products. The action of sulphuric acid as an absorbent and polymerising agent has been used to determine the unsaturated and aromatic classes. Iodine and bromine absorption values have been used to determine unsaturates and to a lesser extent aromatics. Nitrating mixtures have been used to determine the aromatic class. The difference in the critical solution temperature with aniline (or nitrobenzene) before and after sulphuric acid treatment has been utilised to estimate the aromatic class.

To a lesser extent physical properties such as refractive index, magnetic rotation, etc. have been used to get a rough estimate of each class.

In their work on aniline points, Tizard and Marshall[1] showed that the paraffins which they examined had an aniline point of 70°C. and that the addition of 1 per cent. of "naphthenes" to these paraffins reduced the aniline point by 0.3°C. These figures are frequently used to determine the napthenes in a motor spirit that has been previously treated to remove unsaturates and aromatics. The above remarks apply chiefly to motor spirit.

In the case of kerosine the estimation of each class has not been so fully investigated, though Carpenter[2] has applied an aniline point method to Burmah kerosine.

One limitation of such work is immediately apparent from the foregoing, namely, the tendency to merging is neglected.

We have considered for some time that a definite advance would be made in estimating the proportion of each class present in a

[1] *J. Soc. Chem. Ind.* **40**, 207 (1921).
[2] *J. Inst. Petr. Techn.* **12**, 518 (1926).

motor spirit and a kerosine if a standard motor spirit and standard kerosine were obtained. The work to be now described was carried out with this object in view.

The most reasonable standard to adopt appeared to us to be a paraffin hydrocarbon standard, both for motor spirit and kerosine, because the paraffins persist through a wide range of petroleum fractions, most physical properties of the isomers are not widely different, and lastly, they are the best known and most fully studied class.

For some time, and unconsciously perhaps, the motor spirit and kerosine fractions of Pennsylvanian crude have been taken as approximately standard because of their high paraffin content, but it is well known that Pennsylvanian oils contain naphthenes. It is also a common practice to subject a motor spirit or a kerosine (particularly the latter) to a heavy sulphuric acid treatment, and consider the so-called "aromatic free" product a Standard, with the knowledge, however, that the Standard contains an unknown proportion of naphthenes. Perhaps the nearest approach to a true paraffin standard motor spirit is Edgar's heptane-iso-octane mixture which is used in anti-knock determinations; but this, being a mixture of two paraffins only, can hardly be called a representative motor spirit.

For the preparation of a standard motor spirit and kerosine, our initial experiments have been directed to the cracking of high melting point refined paraffin wax from Burmah crude.

This wax, as far as analysis shows, was practically pure paraffin and contained only a small percentage of oil. The effect of cracking was to form a product from which motor spirit and kerosine could be obtained. This product according to the method of cracking might contain some or all four of the main classes of hydrocarbons. It is certain that whatever the method of cracking, the paraffin and unsaturate classes will be represented. The aromatic class will be present if the method is one in which high temperatures (and pressures) are used. Naphthenes are produced to a greater or less extent in those methods which tend to the formation of members of the aromatic class.

Unsaturated and paraffin hydrocarbons predominate when the method employs lower temperatures (and pressures) and the decomposition products are removed shortly after they are formed, as in "pressure distillation." It is very uncertain whether naphthenes are formed from paraffin wax in this latter method of cracking, the only possible way being the secondary reaction of cyclic condensation of small unsaturated molecular fragments produced by decomposition of the large molecules comprising the paraffin wax. If the cracked products are removed as fast

as they are formed, the production of naphthenes will tend to a minimum. Experimental results show that practically no members of the aromatic class are produced by this method of cracking, so that the effect of a pressure distillation on paraffin wax at moderate temperature and pressure gives a product containing chiefly unsaturates and paraffins, and possibly naphthenes.[3]

For this reason we adopted the pressure distillation method for cracking the high melting-point Burmah wax. (While this work was in progress results on the cracking of a paraffin wax have been recorded by Sachanew and Tilitscheyew.[4] They investigated the cracked products and concluded that the motor spirit fractions contained no naphthenes. They derived this from the results of Egloff-Morrel analysis and critical solution temperature in aniline, methods which, though useful, are not accurate enough to warrant such a conclusion.)

The wax had the following characteristics :—

Specific gravity (solid) (approx.)	0·8965
Melting point	141° F.
Oil in wax	1·2%
Ultimate Analysis.	
Carbon	85·25%
Hydrogen	14·75%
Molecular weight	425

From the above, the average empirical formula is almost exactly $C_{30}H_{62}$, which is of the C_nH_{2n+2} or paraffin series.

The cracking operations were carried out in a vertical autoclave of 3½ litres total capacity. In each operation the autoclave was charged to about two-thirds of its volume with the melted wax. It was closed by a flange carrying a thermometer pocket and junction piece. The latter was fitted with a pressure gauge and needle valve. Heat was supplied by a large gas burner. When the pressure reached the required value (in all our experiments it was 100 lb.) the needle valve was opened and the products of decomposition passed through a condensing system to a receiver. The uncondensible gas passed through 800 cc. wash oil (ice cooled) to a meter, and finally through a Drechsel flask containing bromine. The needle valve and burner were adjusted so that the distillation proceeded at a moderate rate while the pressure remained constant at 100 lb. When no more distilled over the pressure was allowed to decrease to atmospheric pressure. The cracking temperature rose from 400° C. to 455° C. during the operation.

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[3] Thorpe and Young, *Ann.* **165**, 1. Brooks and Humphrey, *J. Amer. Chem. Soc.* **38**, 393. Egloff and Twomey, *J. Phys. Chem.* **20**, 515.

[4] *Petroleum Zeitschrift*, **23**, 521 (1927).

The condensate or pressure distillate collected in the receiver was redistilled over a ring packed Hempel column, and the following fractions were taken :—

(*a*) Distillate to 150° C. or Motor Spirit fraction.
(*b*) Distillate 150° C. to 285° C. or Kerosine fraction.
(*c*) Residue.

The last fraction or residue will not be considered in this paper, but will be the subject of a future paper. The separation and identification of the bromides formed by the action of the uncondensible gas on bromine will also be reported on at a future date.

The following figures are representative of the cracking operations carried out :—

Charge	1855 gms.	
Cracking pressure	100 lb.	
Cracking temperature	400° C.—455° C.	
Time at cracking pressure	2 hours	
		Sp. gr. at 60° F.
Pressure distillate	2255 ccs.	0·753
Uncondensible gas	70 litres	
Coke	8 gms.	
Distillate to 150° C.	710 ccs.	0·702
Distillate 150° C. to 285° C.	1085 ccs.	0·7755
Residue	355 ccs.	0·8195

The wash oil removed 75 ccs. of light spirit (specific gravity 0.644) from the uncondensible gas.

Some characteristics of the motor spirit and kerosine fractions are shown in the following :—

Motor Spirit Fraction.		Kerosine Fraction.	
Sp. gr. at 60° F.	0·702	Sp. gr. at 60° F.	0·7755
Colour	Very pale yellow	Colour	Intense lemon yellow
Aniline point	44·6° C.	Aniline point	69·5° C.
I.B.P.	27° C.	I.B.P.	143° C.
Distillate below 50° C.	3%	Distillate below 175° C.	7%
„ 75° C.	20%	„ 200° C.	30%
„ 100° C.	48%	„ 225° C.	55%
„ 125° C.	77%	„ 250° C.	79%
„ 150° C.	92·5%	„ 275° C.	95%
F.B.P.	158° C.	F.B.P.	287° C.
Total distillate	95%	Total distillate	98·5%

It is interesting to note at this stage that in the distilling over of the motor spirit fraction of the pressure distillate, at a still head temperature of 110°C.—120°C. the condensate began to show a pale yellow colour. This is unusual, for in the case of most unrefined pressure distillates this colour does not appear in the condensate until the still head temperature is about 150° C. and even higher.

The next stage in the preparation of the paraffin standards was the refining of the motor spirit and kerosine fractions of the pressure distillate. These fractions contained members of the unsaturated and paraffin classes, and possibly naphthenes. It was decided to use sulphuric acid for the initial method of refining.

The investigation of the action of sulphuric acid on petroleum fractions has received much attention, and, as far as possible, the results of such work were taken as a basis of the procedure adopted.

The action of sulphuric acid on members of the paraffin class has not been effectively studied, but the general opinion appears to be that acid of less than 100 per cent. strength at ordinary temperature has practically a negligible absorptive and reactive effect : naphthenes approach closely to paraffin in this respect.

The effect of sulphuric acid on unsaturated hydrocarbons and petroleum distillates containing the same has been frequently recorded, but the results give only a very general idea of the reactions. Brooks and Humphrey[5] have shown that the degree of polymerisation tends to increase with increasing sulphuric acid concentration ; also that a higher yield of the alkyl sulphuric esters (and, therefore, less polymerisation) takes places at low temperatures. Further, polymers, when formed, are more stable towards sulphuric acid than the parent unsaturate. Michael and Brunel[6] observe that, generally, with increasing molecular weight of the unsaturate, the greater is the tendency to polymerise. It is obvious that the ideal treatment would give a 100 per cent. formation of the alkyl sulphuric esters, because the polymerised bodies are of unknown constitution and appear to be more stable towards acid. Also, the esters were required for further investigation. Of these the mono-alkyl esters are more or less removed by water, but the di-alkyl esters are sparingly soluble in aqueous solutions, but are easily soluble in oil. They are removed more or less efficiently by steam distillation but decompose during the process with evolution of sulphur dioxide.

Recently Ormandy and Craven[7] have described work tending to show that sulphuric acid is capable of condensing olefines to saturated open chain paraffins of higher boiling points. Whether this actually happens remains to be investigated, but at any rate is favourable to the work described here.

We have been unable to find experimental evidence in the literature that the polymerisation of unsaturated hydrocarbons by sulphuric acid produces naphthenes, so have concluded that none are forming in our refining. Therefore, in the light of the

[5] *J. Amer. Chem. Soc.* **40**, 822 (1918).
[6] *J. Amer. Chem. Soc.* **48**, 267–79 (1926).
[7] *J. Inst. Petr. Techn.* **13**, 311 (1927).

above mentioned work, conditions of refining were adjusted as follows :—

(1) Treatment of each fraction with gradually increasing concentrations of acid.

(2) Treatment at a low temperature.

Since the two fractions required somewhat different treatments they are described separately below. The refining of the motor spirit fraction was as follows :—

(i) 15 mins. wash with 0·5 vol. 70 per cent. acid—settle—separate.
(ii) 15 mins. wash with 0·5 vol. 80 per cent. acid—settle—separate.
(iii) 15 mins. wash with 0.5 vol. 90 per cent. acid—settle—separate.
(iv) 15 mins. wash with 0·5 vol. water—settle—separate—filter.

At this stage the spirit was yellowish brown in colour, and the washing had been carried out at laboratory temperature.

(v) 30 mins. wash with 1 vol. 96 per cent. acid—settle—separate.
(vi) 15 mins. wash with 1 vol. water—settle—separate.
(vii) 15 mins. wash with 0·5 vol. 10 per cent. soda—settle—separate—filter.

Stages (v)-(vii) were carried out in an open vessel fitted with a mechanical stirrer and cooled with ice. The light end of the spirit was partly lost at this stage by evaporation. The spirit was water white and its specific gravity had increased from 0·702 to 0·7605. This showed that the spirit contained a high proportion of polymers, or alkyl esters, or both, which were colourless. The spirit was distilled up to 150° C. using the Hempel column and 54 per cent. distillate was obtained ; the residue (approximately 46 per cent.) was coloured light brown because of decomposition taking place during the heating with evolution of sulphur dioxide. The 54 per cent. distillate had a specific gravity of 0.705 and was washed with soda and water before being given further treatment.

(viii).—15 minutes wash with 0·5 vol. 100 per cent. acid—settle—separate.
(ix).—30 minutes wash with 0·5 vol. 100 per cent. acid—settle—separate.
(x).—15 minutes wash with 0·5 vol. water—settle—separate.
(xi).—15 minutes wash with 0·5 vol. soda—settle—separate.
(xii).—Steam distilled.

Stages (viii)–(xi) were carried out at the temperature of ice water. In the steam distillation practically all the spirit distilled over colourless. The total loss on the refining was somewhere between 60 and 70 per cent., this included the heavy evaporation loss due to the open method of washing the spirit with acid. This latter loss will be minimised in future work by the use of a special closed-in apparatus.

The refined spirit had the following characteristics :—

Sp. gr. at 60° F.	0·708
Aniline point	68·1° C.
I.B.P.	66° C.
Distillate below 100° C.	8%
„ 125° C.	70%
„ 150° C.	96·5%
F.B.P.	155° C.
Total distillate	99%

In the refining of the kerosine fraction the method adopted consisted of slowly adding cooled acid of the required strength and volume to the kerosine contained in a mixer at 0° C. and then separating the acid tar, and repeating the procedure with more concentrated acid, the final treatment being performed with acid of 100 per cent. strength.

When a small portion of the kerosine fraction after treatment with 90 per cent.–96 per cent. acid was washed with water and soda in the usual manner, an emulsion formed which was difficult to break down. This difficulty was overcome as follows :—the acid treated oil was agitated with 5 per cent. of an absorbent clay (" Anglobit ") then filtered from the clay. This efficiently removed those substances which caused emulsification.

It was found that an acid of strength under 85 per cent. had only slight action on the kerosine fraction, hence 85 per cent. was the initial concentration of acid used. The acid tar, produced during each treatment, was poured on ice, and the product boiled with soda, and distillated with superheated steam. The distillate has been retained for subsequent work.

The treatment and losses in refining the kerosine fraction are shown as follows :—

Treatment.	Loss %	Sp. gr. at 60° F.
0·5 vol. of 85% acid	3·8	—
0·5 vol. of 90% acid	3·8*	—
0.5 vol. of 96% acid	27·0	—

* The action of 90% acid, both on the petrol and kerosine fractions, is very different from the action of acid of any other strength. Sulphur dioxide is copiously evolved, and the temperature of the liquid rises quickly unless efficient cooling is provided. The acid treated oil is darker in colour than the spent acid which is the reverse of what usually happens.

Treatment.	Loss %	Sp. gr. at at 60° F.
5% of clay (" Anglobit ")	3·2	0·807
0·5 vol. of 100% acid	11·1	—
5% clay (" Anglobit ")	3·0	—
0·5 vol. of 100% acid	2·2	—
Water and soda washes	1·3	0·777
Steam distillation until distillate was off colour..	16·2	—
0·5 vol. of 100% acid	0·5	—
Water and soda washes	1·1	0·764

The total loss on the refining of the kerosine fraction as shown above was 73·2 per cent. The refined kerosine had the following characteristics :—

Sp. gr. at 60° F.	0·764
Aniline point	82·5° C.
I.B.P.	157° C.
Distillate below 175° C.	2·5%
„ 200° C.	21·5%
„ 225° C.	56·0%
„ 250° C.	82·5%
„ 275° C.	96·0%
F.B.P.	292° C.
Total distillate	98·5%

The kerosine was water white and the smell generally associated with " aromatic free " kerosine was entirely absent.

The refined motor spirit and kerosine fractions were each subjected to fractional distillation over a ring packed Hempel column and 10° C. fractions were collected.

The following physical properties of each fraction were determined.

(1). Specific Gravity at 60° F. and 20° C.

(2). Aniline Point (i.e. the solution temperature of the fraction mixed with an equal volume of aniline).

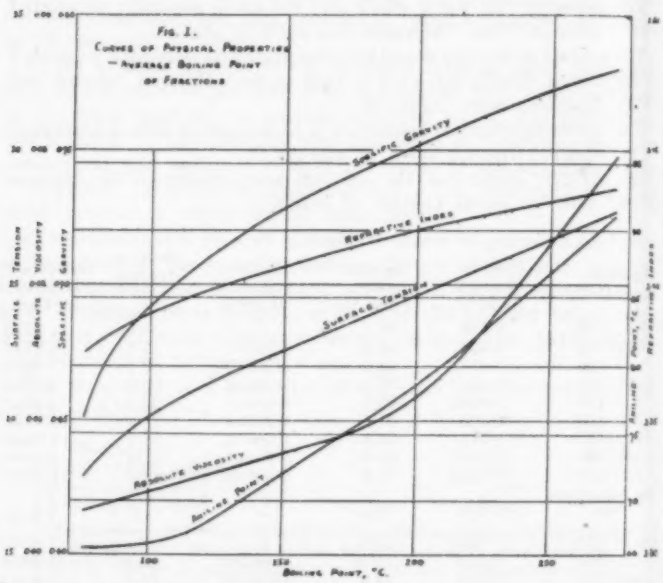
TABLE I.

Fraction Deg. C.	Specific gravity at 20°C.	Aniline point, deg. C.	Absolute viscosity at 20°C.	Surface tension at 20°C. dynes/cm.	Refractive index at 20°C$_{ND}$.
I.B.P.– 70	0·639	66·5	—	—	1·3726
70– 80	0·651	66·5	0·00332	17·9	1·3753
80– 90	0·678	66·7	0·00369	19·1	1·3827
90–100	0·687	66·8	0·00446	19·9	1·3865
100–110	0·6965	66·9	0·00471	20·3	1·3901
110–120	0·705	67·5	0·00558	21·0	1·3933
120–130	0·713	68·8	0·00577	21·5	1·3990
130–140	0·7195	69·7	0·00641	21·9	1·4018
140–150	0·7265	71·3	0·00750	22·3	1·4068
Residue above 150	0·729	72·8	—	—	1·4101
I.B.P.–150	0·7215	70·6	—	—	1·4042
150–160	0·729	72·5	0·00760	22·9	1·4084
160–170	0·733	73·8	0·00751	23·1	1·4102
170–180	0·739	75·3	0·00895	23·6	1·4135
180–190	0·744	76·8	0·01026	24·1	1·4161
190–200	0·748	78·1	0·01137	24·6	1·4187
200–210	0·752	79·4	0·01222	24·8	1·4208
210–220	0·757	80·7	0·01410	25·2	1·4231
220–230	0·762	82·5	0·01574	25·5	1·4250
230–240	0·767	84·3	0·01924	26·0	1·4270
240–250	0·769	85·9	0·01996	26·5	1·4293
250–260	0·774	87·6	0·02406	26·8	1·4320
260–270	0·777	89·3	0·02687	27·3	1·4336
270–280	0·780	91·0	0·02975	27·7	1·4353
Residue above 280	0·794	92·0	0·03200	28·5	1.4420

(3) Refractive Index at 20°C. for the sodium D line using the Pulfrich refractometer.

(4) Absolute viscosity at 20°C. using Thole viscometers calibrated against liquids of known absolute viscosity. Two such viscometers covered the entire range.

(5) Surface Tension at 20°C. by the capillary rise method. Two capillaries were used, their diameters being measured by a microscope every 45° and the mean diameter taken. The capillary rise was measured by a travelling microscope and the result given is the average for a determination with each tube.



The results obtained are set forth in Table I. Data on physical properties of paraffin and naphthene hydrocarbons form Tables II and III; these were compiled from the literature, the chief sources being Day's Handbook, Brooks' Non-benzenoid Hydrocarbons, Das Erdöl and International Tables of Physical and Chemical Constants. Figure I is a graphical representation of Table I.

The first feature of interest in Table I is the very low specific gravities of the fractions. Besides paraffin hydrocarbons some

TABLE II.

Hydrocarbon.	Boiling point, deg. C. (760 mm.).	Spec. grav. at 20°C.	Refractive index at 20°C$_{ND}$.	Absolute viscosity at 20°C.	Surface tension at 20°C.
n-pentane	36	0·6290		0·00232	
iso-pentane	28	0·632		0·00204	
n hexane	69	0·6595	1·376	0·00320	17·4
2-methyl pentane	62	0·661	1·372	0·00371	
3- " "	64	0·668	1·377		
2.2-dimethyl butane	49·6	0·649	1·369		
2.3- " "	58	0·666	1·3783		
n-heptane	98·5	0·683	1·385	0·004105	19·2
2-methyl hexane	90	0·680			
3- " "	91	0·683			
2.2-dimethyl pentane	78·5-79·0	0·6765			
2.4- " "	83–84	0·686	1·3825		
3.3- " "	86–87	0·6755			
2·2·3-trimethyl butane	81	0·689	1·390		
3-ethyl pentane	95–98	0·7005	1·393		
n-octane	125	0·7025	1·398	0·00538	
2-methyl heptane	116	0·704	1·3965		
3- " "	117·5	0·713	1·4035		
4- " "	118	0·718	1·3980		
2·3-dimethyl hexane	114	0·721	1·4095		
2·4- " "	110	0·706	1·4026		
2·5- " "	108	0·697	1·3929		
3·4- " "	116·5	0·725	1·4058		
3-ethyl hexane	119	0·7155	1·4016		
2-methyl 3-ethyl pentane	114	0·7060	1·4017		
2·2·3-trimethyl pentane	110·5	0·7185	1·4186		
n-nonane	150	0·7150	1·4050		21·9?
4-methyl octane	142	0·7295	1·4047		
2·4-dimethyl heptane	133	0·7185	1·4038		
2·5- " "	135–136	0·717	1·4040		
2·6- " "	132	0·710			
4-ethyl heptane	139	0·741	1·4080		
n-decane	173	0·7304	1·415		
2-methyl nonane	160	0·725	1·408		
3- " "	167	0·735	1·4126		
5- " "	166	0·732	1·4116		
2·6-dimethyl octane	173–174	0·732	1·411		
2·7 " "	161	0·762	1·408		
4-propyl heptane	161·5	0·736	1·414	0·00817	
n-undecane	194	0·741	1·4184		
5-ethyl nonane	71 (16 mm.)	0·751			
n-do-decane	214	0·751	1·4208		
5·6-dimethyl decane	190	0·751			
5-propyl nonane	205	0·756	1·4228		
n-tridecane	234	0·760	1·4401		
4-propyl decane	221·2	0·758	1·427		
5-butyl nonane		0·760	1·427		
Tetradecane	252·5	0·764	1·4459	0·02180	
Pentadecane	270·5	0·769	1·4413	0·03341	
Hexadecane	287	0·7805	1·4413		
Heptadecane	303	0·778	1·4376		
Octadecane	317	0·8015	1·440		

TABLE III.

Hydrocarbon.	Boiling pt. deg. C.	Spec. gr. at 20°C.	Refractive index at 20°C$_{D}$.	Absolute viscosity at 20°C.
1·1·2-trimethyl cyclopropane ..	60	0·692	1·3848	
1·2·3- „ „ ..	79	0·6925	1·3949	
Methyl cyclobutane	45	0·751		
Ethyl „	72	0·748	1·4094	
Diethylmethylcyclobutane ..	150	0·788	1·4298	
Cyclo pentane	49	0·7505	1·4086	
Methyl cyclo pentane	72–73	0·7500	1·4101	
1·1-dimethylcyclopentane ..	92	0·742	1·4131	
1·2- „	92	0·7532	1·4126	
n-propyl cyclobutane	100	0·744	1·4119	
1·3- „ „	94	0·7595	1·4130	
1-methyl 2-ethylcyclopentane ..	124			
1- „ 3- „ ..	121	0·7663	1·4216	
Cyclo hexane	80	0·779	1·4258	
Methyl cyclohexane	100	0·769	1·4243	
1·1-dimethyl cyclohexane ..	102	0·773	1·4232	
1·2- „ „ ..	123	0·768	1·4239	
1·3- „ „ ..	120	0·764	1·4179	
1·1·3-trimethylcyclohexane ..	118	0·742	1·4318	
1·2·4- „ ..	135	0·7665	1·4244	
1·4-dimethyl cyclohexane ..	120–121	0·769		
Ethyl cyclohexane	130	0·711	1·4325	0·00895
1·3·4-trimethyl cyclohexane ..	140	0·789	1·4330	
1·3·5- „ „ ..	134–136	0·779	1·4262	0·00682
1-methyl-2-ethyl cyclohexane ..	148	0·7891	1·4351	
1 „ 4- „ „ ..	150			
1·3-diethyl cyclohexane.. ..	170	0·7955	1·4388	
n-propylcyclohexane	150	0·767		
iso „	140	0·787		
1·isopropyl-2-methylcyclohexane	171	0·8135		
1- „ 3- „	166	0·797		
1- „ 4- „	167	0·803		
1·3-dimethyl-5-ethylcyclohexane	168	0·797		
Isobutyl cyclohexane	157	0·804	1·4444	0·01223
1-methyl 3-ethyl 4-isopropyl cyclohexane..	220	0·8146		
2·6·6-trimethyldicyclohexane ..	140	0·8225		
3·3-dimethyldicyclohexane ..	115	0·796	1·4331	
2-cyclohexyl 2-methylbutane ..	191–192	0·8195		
3- „ 2- „ pentane ..	206–207	0·834		
3- „ 3- „ „ ..	207–208	0·828		
3- „ 3-ethyl „ ..	222–223	0·836		
3- „ 3-methyl hexane ..	224–226	0·8375		
Tetralin	205–207	0·9715		
Dekalin	189–191	0·8827		
αα dicyclohexylethane	256–257	0·9271	1·511 (40°)	

members of the unsaturate class possess low specific gravities, but since the refined motor spirit and kerosine fractions gave no reaction for unsaturates, the presence of the latter was ruled out. Naphthenes have higher specific gravities than the paraffins. The position the fractions take among the classes of hydrocarbons with regard to specific gravity is best shown by the specific gravity-

boiling point curves* of Figure II ; these were drawn from the data of Tables I, II and III. It was only possible to obtain an approximate curve for naphthenes, and it will be seen it was impossible to make a satisfactory curve for branch chain paraffins. However, the graph does show that the specific gravities of our fractions are much lower than those of naphthenes, and higher than

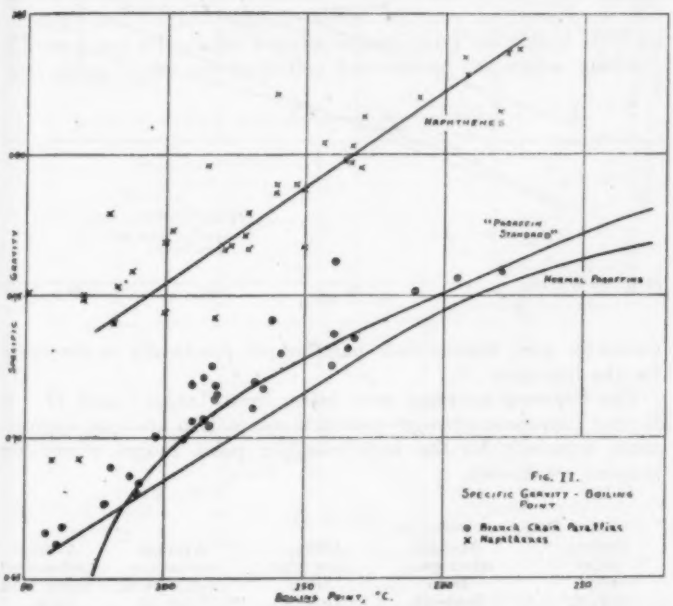


FIG. II.
SPECIFIC GRAVITY - BOILING POINT
○ BRANCH CHAIN PARAFFINS
× NAPHTHENES

those of normal paraffins. The specific gravities of most of the branch chain paraffins shown on the graph are nearly the same as those of the fractions.

In a similar manner the refractive index—boiling point curves* were constructed, and are shown in Figure III. Here, as in the case of specific gravity, the refractive indices of the fractions approximate to those of the normal and branch chain paraffins,

* The "Paraffin Standard" curve was obtained by plotting the physical property of the fraction against the mean of the cutting temperatures of the fraction ; this procedure is only approximately correct.

and are considerably lower than those of the naphthene hydrocarbons. Figure V gives the graphical relation between the specific gravity and the refractive index, and is free from the approximation stated in the footnote. It shows that the fractions give a curve situated between the corresponding curves for normal paraffins and naphthenes, being nearer to the former. As in Figure II the

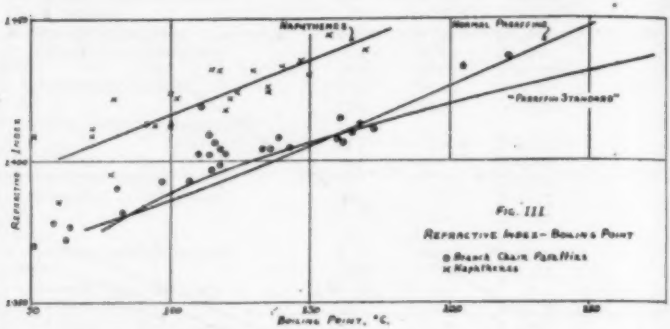


FIG. III.

REFRACTIVE INDEX—BOILING POINT

⊙ Branch Chain Paraffins
× Naphthenes

values for most branch chain paraffins are practically on the curve for the fractions.

The following averages were taken from Tables I and II. It is clear that these averages and their comparison are only approximate, especially for the higher boiling point ranges where few isomers are known.

TABLE IV.

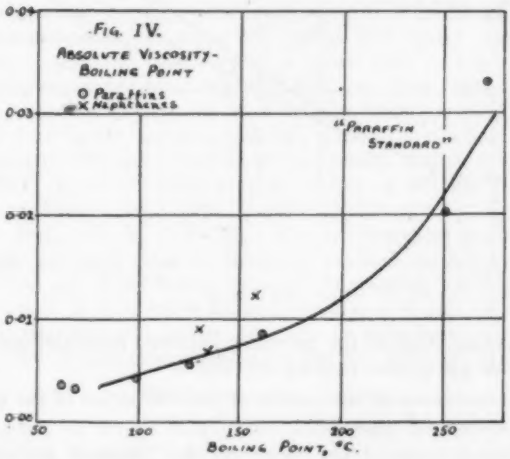
Boiling point range, deg. C.	Average spec. grav. from Table II.	Average spec. grav. from Table I.	Average refractive index from Table II.	Average refractive index from Table I.
70– 80	0·673	0·651	1·381	1·375
80– 90	0·684	0·678	1·388	1·383
90–110	0·693	0·692	1·396	1·386
110–120	0·712	0·705	1·404	1·393
130–140	0·722	0·7195	1·405	1·402
160–170	0·738	0·733	1·412	1·410
190–200	0·741	0·748	1·418	1·419
200–210	0·758	0·752	1·418	1·421

The above comparison is based on the assumption that each boiling point range of the paraffins is a mixture of equal parts of the isomers given in Table II. The agreement, however, is extremely good. The fact that the specific gravities and refractive indices of the fractions are nearly all slightly lower is interesting,

since the presence of naphthenes would tend to raise them above the average values for paraffins.

Figure IV shows the absolute viscosity-boiling point curve (see footnote, page 489) of the fractions, together with the few values of the viscosity of pure hydrocarbons existing in the literature. As far as it goes the curve is practically coincident with the viscosity values of the paraffins.

Only two surface tension values of pure hydrocarbons (*i.e.* n-hexane and n-heptane) were found, and these are almost identical with those of the corresponding fractions of the motor spirit.



The aniline points shown in Table I are much higher than those of corresponding petroleum fractions, and are in accordance with previous work done on the subject.

The above survey of the physical properties of the fractions and their comparison with the corresponding properties of those hydrocarbons given in Tables II and III leads to the conclusion that the motor spirit and kerosine prepared and refined, as has been described, are practically pure paraffins. It also shows that this motor spirit and kerosine are composed of branch chain paraffins, rather than normal paraffins, though the latter are almost certain to be present.

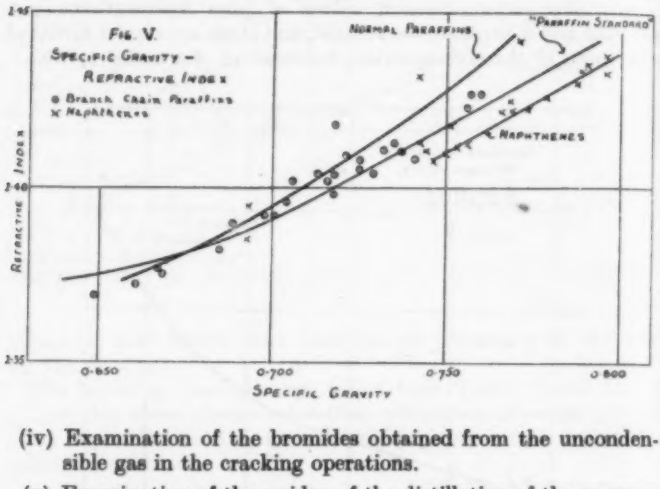
Part II of this series will deal with the comparison of motor spirit and kerosine from other sources with the paraffin motor spirit

and kerosine described above. Future work on this subject will be directed to the following :—

(i) Cracking of other wax fractions.

(ii) Other methods of refining the pressure distillate.

(iii) Examination of the polymers etc. formed in the sulphuric acid treatment of the pressure distillate.



(iv) Examination of the bromides obtained from the uncondensible gas in the cracking operations.

(v) Examination of the residue of the distillation of the pressure distillate (*cf.* page 481).

(vi) Examination of the effect on the physical properties of the paraffin motor spirit and kerosine by the addition of aromatic and naphthene hydrocarbons.

In conclusion, the authors wish to thank Mr. W. J. Wilson, F.I.C., for the interest he has taken in this work, and to the directors of The Burmah Oil Co., Ltd., for permission to publish this paper.

The Examination of a Nigerian Lignite and the Isolation of Montan Wax.*

By Charles Edmund Wood, M.Sc., A.I.C. (Member), and Sydney Diggary Nicholas, B.A., A.I.C.

Considerable interest has been aroused recently with respect to the utilisation of the various extensive lignite deposits in Nigeria. The deposits have been described in the *Miscellaneous Series of Colonial Reports* on the mineral survey of Southern Nigeria, which survey was initiated by the Imperial Institute as early as 1903. The preliminary investigations were completed in 1913 (Colonial Reports—*Miscellaneous Series* [Cd. 2876], [Cd. 4994], [Cd. 4995], [Cd. 5901] with the discovery of a great coal field at Udi, an interesting account of which is given (*Bull. Imp. Inst.*, 1916, 14, 369). This important discovery diverted interest from the neighbouring West African lignite deposits, and only within the last two or three years has attention been directed to the problem of their commercial value (*Bull. Imp. Inst.*, 1923, 21, 325; 1925, 23, 202; R. C. Wilson in occasional paper No. 1, 1924 [Revised Edition, 1925]; *Geol. Surv. Nigeria, Bull., No.* 8, 1925, 79). The experimental work carried out so far indicates that the lignite is suitable, on account of its composition and high calorific value for briquetting, while the data, though small, is favourable for the production of gas, oil and tar, although the chemical nature, phenolic or otherwise, of the products of low temperature distillation has not been investigated.

Nature of the Lignite.

The lignite or brown coal showed somewhat indistinct lamination. It was markedly heterogeneous. The bulk of it was brown of various shades, had a dull, earthy texture and appeared to contain fine elastic particles.

The various more definite bodies that it contained exhibited a tendency to parallel arrangement marking a lamination and indicating the stratification of the coal. The most conspicuous of these brighter, darker (brownish-black), more homogeneous bodies, elongated-lenticular in section are evidently the remains of the wood of individual plants. One of these appeared to exhibit woody texture. Another lenticular section measured about 24 x 5 millimetres and exhibited a thin, bright black "cortex" ½ mm. thick and an interior of dull dark brown material, representing softer internal tissues. Other bodies varied from light brown to bright ochre yellow and had the appearance and behaviour of

* Paper received May 17, 1928.

mineral waxes. Others, again, had the vitreous lustre, amber colour and transparency of resin and are probably of that nature.

The lignite exhibited abundant shrinkage cracks which were especially conspicuous in the black, more homogeneous lenticles. Probably in the dull brown matrix the corresponding shrinkage is inconspicuous owing to it being more evenly distributed between the fine particles of which the matrix consists.

The lignite was free from earthy and mineral impurity, gives a polish on rubbing and can be easily powdered. It ignites fairly readily and burns with a steady luminous flame, giving off only a small amount of smoke. It does not cake or decrepitate on heating.

Three typical analyses corresponding to Samples I., II. and III. are given below :—

Samples :	I.	II.	III.
	%	%	%
Volatile Matter	50·65	55·28	49·0
Fixed Carbon	24·95	19·72	21·75
Ash	4·90	5·03	5·55
Nitrogen*	0·875	0·899	0·847
Sulphur†	0·628	0·671	0·602
Water‡	19·5	19·97	23·70
Density	1·246	1·209	1·203

The three analyses show that the lignites investigated were slightly different and representative of a good lignite. They have high volatile matter, low ash, fixed carbon and nitrogen of average value, small sulphur content and a fairly high percentage of moisture (due to the fact that it has not been allowed to dry thoroughly in the air). The density varies slightly from about 1·2 to 1·31, with an average value of about 1·22. These samples are remarkable for their high volatile matter, extraordinary low percentage of ash and small sulphur content.

As a point of interest the results of the analyses of samples of lignite from the Okpanam-Ibusa district (*Bull. Imp. Inst.*, 1923, loc. cit.) are given.

Samples from the Atakpo Valley, Okpanam.

	Average.	Best.	Consignment of 10 tons.	The consignment dried to 10% moisture (calculated).
	%	%	%	%
Volatile Matter ..	44·86	52·86	42·36	52·53
Fixed Carbon ..	29·48	33·28	25·84	32·04
Water	11·81	8·90	27·42	10·0
Ash	13·85	4·96	4·38	5·43
Sulphur	1·10	0·54	—	—

* Determined by the methods of Kjeldahl and also Dumas.

† Estimated by means of method described (*U.S.A. Bureau of Standards*, Tech. paper, No. 117).

‡ Determined by means of two methods: (*a*) Loss in vacuo at 110° C.; (*b*) Method described *Jour. Inst. Pet. Tech.*, 1925, Vol. XI, 471.

Our results for samples I., II. and III. averaged and calculated to 10 per cent. moisture content for comparative purposes are given below :—

Average Values.

	%
Volatile Matter	58·87
Fixed Carbon	25·24
Water	10·00
Ash	5·88
Sulphur	0·72

The analytical resemblance of the two lignites is interesting.

Extraction of Bitumen or Wax by Means of Solvents.

The lignite on extraction with certain solvents gave a considerable yield of bitumen and the following were tried qualitatively : ethyl, alcohol, methyl alcohol, acetone, methyl ethyl ketone, ether,carbon tetrachloride, chloroform and light petroleum (boiling point up to 80° C.), but the wax was not sufficiently soluble to warrant quantitative determinations. Various methods of extraction were tried, but owing to the very large number of estimations necessary the method by means of a Soxhlet's extractor, which combined convenience with accuracy, proved the best. The Soxhlet was jacketed with asbestos and this promoted considerably the action of the solvent. Extractions in duplicate or triplicate were carried out under precisely the same conditions.

The lignite was used in a powdered form and passed through a sieve (30 mesh).

Sample 1.

(Dried at 100-105° C., moisture content 1·85%.)

Extraction 20 hours with a Soxhlet's Extractor.

Solvent	% wax on air dried sample.	Melting point of wax isolated. ° C.	% wax calculated to anhydrous lignite.	% wax calculated to original lignite.
Toluene	10·59	84-87·5	10·8	8·7
Xylene	10·7	84-88	10·9	8·6
Light petroleum ..	7·04	88 sharp	7·2	5·8
Butyl alcohol ..	12·82	84-88	13·1	10·5

The table shows that butyl alcohol was the most efficient solvent, yet toluene and xylene were excellent extractors. Light petroleum was the poorest solvent of all. Although only one result is recorded here, a number of experiments were done using light petrols of different boiling point ranges.

The wax has a high melting point for a montan wax and melts either sharply or over a very close range of temperature. This sample has a lower wax content than the other two samples examined.

Sample II.

(Dried at 100-105° C, moisture content 2%.)

Extraction 20 hours with a Soxhlet's Extractor.

Solvent.	% wax on air dried sample.	Melting point of wax isolated ° C.	% wax calculated to anhydrous lignite.	% wax calculated to original lignite.
Benzene	15·5	88-90	15·8	12·6
Toluene	16·3	85-88	16·7	13·4
Xylene	17·3	85-87·5	17·7	14·2
Butyl alcohol ..	21·9	88-89	22·4	17·9
Amyl alcohol ..	16·7	88-90	17·0	13·6

The series of solvents, benzene, toluene and xylene increase in efficiency with rise of boiling point; moreover, they possess the advantages of ready elimination from the residual wax and commercial cheapness. Owing to their non-miscibility with water these solvents could not be used with undried lignite in the laboratory method adopted. This difficulty does not occur with butyl alcohol, for it is miscible to a considerable extent with water. Further, butyl alcohol is miscible in all proportions with benzene, toluene or xylene, and this mixture will take up water, the quantity of water dissolved increasing, *pari passu*, with the increasing amount of butyl alcohol in the mixture, so such a mixture should prove an efficient solvent for the wax in the undried lignite. Amyl alcohol, since it has a higher boiling point than butyl alcohol, was tried but did not prove so efficient as the latter, this being due possibly to the lower solubility of water in amyl than in butyl alcohol. The efficiency of extraction depends on (*a*) solvent action of the liquid used as solvent, (*b*) temperature of extraction, (*c*) pressure under which the extraction is carried out, (*d*) time of extraction and (*e*) the miscibility of the solvent with the water in

Sample III.—Extraction.

Solvent.	% water in Sample.	Time in hours.	Melting point of wax.	% wax calculated to anhydrous lignite.	% wax calculated to original lignite.
Butyl alcohol ..	12·3	10	89-92°	12·6	9·9
Butyl alcohol ..	12·3	15		18·2	14·3
Butyl alcohol ..	23·7	28		23·2	17·7
Butyl alcohol ..	23·7	32		25·5	19·5
Butyl alcohol ..	1·79*	20	89-91°	24·0	18·3
Westron	1·79*	20	No definite melting point.	24·7†	18·9†
Butyl alcohol 10% / Toluene 90%	1·79‡	20	87°	17·75	13·5

* Dried at 100-105° C.

† Extracted matter had not the properties of a wax and contained chlorine from the westron. It did not give a definite melting point and had a charred appearance.

‡ Shows influence of mixed solvent.

the lignite. Extraction in the laboratory generally is considerably less efficient than on a works scale, so that the percentages recorded represent minima rather than maxima values of the wax obtainable.

The outstanding feature is the high extraction effected by means of butyl alcohol, but it cannot, however, compete in commercial cheapness with either benzene, toluene or xylene.

The above results show that butyl alcohol, owing to its miscibility with water is equally effective both with undried and dried lignite. Also the extraction is practically complete after twenty hours contact with the solvent; especially is this the case with dried lignite. Although butyl alcohol is superior as an extractor, yet it is difficult to remove the last traces of the alcohol from the wax, and unless the last traces are removed the hardness and melting point of the wax are lowered.

Westron at ordinary temperature dissolves the wax more readily than ether, chloroform or carbon tetrachloride, but owing possibly to chemical reaction and simultaneously the high temperature of extraction, the properties of the extracted wax were completely changed. The following is a record of data concerning the solvents used :—

	Boiling point range.	Boiling point chief fraction.
Xylene	130-138° C.	136°
Benzene	78-81°	80°
Butyl alcohol ..	110-117°	114°
Petroleum ether ..	126-134°	129°
Toluene	107-111°	107°
Amyl alcohol ..	124-135°	127·5°
Westron	137-157°	142-149°

In comparison with this Nigerian lignite it is interesting to note that the lignites of Saxony-Thuringia are quoted as yielding 5-10 per cent. bitumen and Meyerheim (*Seifenfahr*, 39 (1919), 365 and 394) quotes 1-27 per cent. as occurring in German Brown coals.

The solvents§ used for extraction of wax from German lignites are benzene, naphthalene, acetone, ketones, ethyl alcohol, petroleum ether and mixtures of certain of these solvents. Although the literature on this subject is overflowing with various extraction patents and processes, yet no case is mentioned of a lignite yielding, by a simple extraction process, a wax of such high grade quality or even in so high a proportion.

Identification of the Isolated Bitumen as Montan Wax.

The wax obtained from lignite is termed crude montan wax (brown coal bitumen wax). The crude wax from the Nigerian

§ Marcusson and Smelkus used benzene under six atmospheres pressure at temperature 260° C. Thuringian lignite yielded wax of melting point 80-90° C.

lignite is dark brownish-black in colour, hard and brittle, breaking with a conchoidal fracture; it has a lustrous appearance and develops a fine hard gloss on rubbing with a cloth. All the specimens of wax obtained from the lignite were capable of being finely powered.

Analytical data available from the literature with respect to crude montan wax (obtained by simple extraction processes) are extremely small. Specimens of commercial crude montan wax and montan pitch therefore were obtained and analysed in order to serve as comparative standards. The analytical results are given below (data for one representative sample of commercial montan wax only being quoted):—

	Montan Pitch Commercial.	Montan Wax Commercial.	Crude Montan Wax.	Crude Montan Wax.‖
Melting Point ..	69–73·5°	70·5–80·5°	84·88°	95·96°
Acid Value ..	25·4	41·3	41·3	68·0
Saponification Value	29·0	138·9	140·5	151·9
Ester Value ..	3·6	97·6	99·2	83·9
Unsaponifiable Matter ..	—	—	—	26%¶
Iodine Value ..	54·0	40·9	48·7	48·4
Lignite sample ..	—	—	I.	I. & II. mixed
Solvent used ..	—	—	Xylene	Butyl alcohol

The analysis given of the wax (xylene solvent) is in remarkable agreement with the commercial standard of montan wax, but the higher melting point, greater hardness and lustre, increased brittleness and higher iodine value, though readily distinguishing it from the commercial standard, classify it as a good mineral wax.

The low melting point, low acid and saponification value of the pitch and increase of iodine value show that it is a very inferior wax.

The analysis given of the wax (butyl alcohol solvent) is interesting, for this wax has a higher melting point and higher acid value than the xylene extracted wax. The higher melting point is due to refining by bauxite. The higher acid value is due to the efficiency of butyl alcohol as a solvent. If the acid present is montanic acid the percentage of montanic acid in the wax is 51·5, the percentage of esters present is approximately 22·5 and of hydrocarbons (alcohols, ketones included under "unsaponifiable matter") 26 per cent.

‖ The wax was dissolved in butyl alcohol, treated with bauxite then the wax recovered from the solvent.

¶ Of high melting point 73-76° C., yellow waxy solid.

The refined montan wax analysed by Ryan and Dillon (*Proc. Roy. Dublin Soc.*, 12, 1909-10, 202) had the following properties :—

Melting Point	76°
Acid Value	73·3
Saponification Value ..	73·9
Ester Value	0·6
Unsaponifiable Matter ..	47% (melt. pt. 58-59° C.)

Since the wax contained no esters, for these are decomposed in general by refining processes, the above authors calculated that the composition of the wax examined was : montanic acid 53 per cent., unsaponifiable matter 47 per cent. This high acid value exemplified both by Ryan and Dillon's and the Nigerian lignite wax is an outstanding feature of a montan wax.

Preliminary investigations on the acid isolated by a modification of the method described by Meyer and Brod *Monat. Chem.*, 1913, XXXIV., 1144) gave a melting point 84-85° C. and a molecular weight (assuming that the acid is monobasic) of 416-420.

Other data available for montanic acid are as follows :—

	Melting Point.	Molecular Weight.
Ryan and Dillon (*loc. cit*)	83° sharp	426
Meyer and Brod (*loc. cit*)	85° about	435-460

The iodine value for the different waxes investigated is sensibly constant.

Further analytical data are given in the table below :—

	Crude Montan Wax obtained from		
Samples :	I.	II.	III.
Melting Point	88-89°	89-92°	89-92°
Acid Value	61	68	48
Saponification Value ..	140	183·5	170·4
Ester Value	79	115·5	122·4
Unsaponifiable Matter ..	—	—	19*
Iodine Value	47-48	—	46·3

These further results confirm the nature of the wax and its high grade quality.

The melting point of crude montan wax as given by different authors varies between wide limits (70-90° C.), and this is due to the fact that the chemical composition of montan wax varies owing to the presence of free acids other than montanic acid, esters of acids of high molecular weight and hydrocarbons ; also an alcohol and a compound of ketonic nature have been signalised.

Examination of the Lignite Ash.

The ash is white to light brown in colour and of a light floury nature ; it contains silicia, ferric oxide, aluminium oxide, calcium oxide, magnesium oxide, alkalies, sulphate and a trace of titanium.

* Melting point 74—76°, yellow waxy solid.

Quantitative Analysis.—The following analyses were done on the moisture and carbon dioxide free ash :—

Lignite Ash Sample :	I.	II.	III.
SiO_2	66·6%	65·71	61·75
Fe_2O_3	10·1	6·52	4·80
Al_2O_3	14·64	20·50	26·86
CaO	2·65	2·51	1·80
MgO	1·22	0·20	0·40
SO_3	3·67	3·45	3·31
Alkalies and Loss	1·12	1·11	1·08

The above results show that the ash is suitable for cement manufacture.

Hydraulic Modulus.—Lime Requirements.—Cement is within specification (British standard specification for Portland cement) if :

$$\frac{CaO}{SiO_2 + Al_2O_3} \text{ is } > 2 \text{ and } < 2{\cdot}85.$$

The amount of lime which should be added to 100 parts lignite ash (calculated on the moisture and carbon dioxide free ash) in order to be within the limits defined for a Portland cement lies between :

Samples :	I.	II.	III.
Lower Limit	140·2 parts	144·8 parts	150 parts
Higher Limit	199·7 „	206·4 „	206·3 „

Considering the following analysis which represents mean values of the above three analyses,

	%
SiO_2	64·69
Fe_2O_3	7·12
Al_2O_3	20·67
CaO	2·32
MgO	0·61
SO_3	3·48
Alkalies and Loss ..	1·11

the amount of lime which can be added to 100 parts lignite ash is between the limits 143·4 and 204·3 parts. If 190 parts of lime were added to 100 parts lignite ash, the composition of the resulting cement by calculation would be as follows :—

	%
SiO_2	22·31
Fe_2O_3	2·45
Al_2O_3	7·13
CaO	66·31
MgO	0·22
SO_3	1·27
Alkalies and Loss ..	0·31

which is within specification.

If the limestone contained silica, ferric oxide, sulphuric anhydride, etc., the quantity of limestone added to the lignite ash before

clinkering could be adjusted so as to bring the resulting cement within the B.S. Specification, for the amount of lime required can be varied between wide limits. A further point to be noted is the low sulphuric anhydride content of the ash.

Conclusions.

1. The results of the forgoing research show that the lignite examined compares very favourably in composition with Nigerian lignites from other districts, which lignites have been proved satisfactory for briquetting.

2. From the lignite considerable yields of montan wax can be obtained by extraction with common solvents; with butyl alcohol 25 per cent. of wax was extracted from one of the samples.

3. The bitumen isolated from the lignite has the properties of a crude montan wax of high melting point and is equal if not better than the commercial sample examined.

4. The composition of the ash shows that it is suitable for cement manufacture.

5. This research aimed at the most efficient laboratory method of procedure for evaluating a lignite (containing montan wax). The methods revealed by a survey of the literature were inadequate. Samples of commercial montan wax had to be procured and analysed to serve as reference standards.

This paper is the outcome of a research undertaken at the request of Messrs. Elder, Dempster and Co., Ltd., who kindly supplied samples of the lignite for investigation and to whom the authors desire to express their thanks.

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REVIEW.

THEORY OF CONTINENTAL DRIFT. American Association of Petroleum Geologists, Tulsa, Okla. $3.50 post free.

This book is a symposium in which a number of authors discuss and criticise Wegener's theory of continental drift and other theories bearing upon the subject.

There is a long and closely reasoned introduction by W. A. J. M. van Waterschoot van der Gracht, who, taking an imperial view, gives a résumé of all relevant facts and hypotheses. For instance, there is to begin with the generally accepted idea that the crust of the earth consists of a shell of "sial" or acid material resting upon a more or less viscose envelope of "sima" or basic material. Then there is the theory of isostasy, dealing with the sinking of thick masses of sial into the sima and the compensating uplifts, following to a great extent the views of Lapworth that each mountain chain or plateau has its corresponding "deep" in the ocean.

The radio-active theory of Joly is also considered as a most important contribution: this postulates a periodical liquification of the sima under thick masses of sial, owing to the accumulation of heat from radio-active sources.

Finally the possible forces affecting continents are closely examined, the tidal forces due to the earth's rotation tending to cause a westward drift, the centrifugal force tending to cause a drift of continental masses towards the equator, and the force of gravity tending to bring about isostatic equilibrium.

The evidences of climates in long past periods, of faunas, of petrographical provinces, are all dealt with, but the author admits quite frankly that on many of the different subjects our knowledge at the present day is by no means sufficient to admit of more than plausible and speculative generalisations.

Van der Gracht deprecates criticism in detail, since our present very imperfect knowledge of the climatic, palæontological and other conditions at the earth's surface throughout geological time do not allow of any attempt being made to give a really accurate history; he is averse to Wegener's suggested wanderings of the poles, but dealing with earth history from the Carboniferous onwards, he is evidently attracted by Wegener's theory of a Pangaea or master continent that broke up, the several parts drifting west, east or south as the case may be, causing at the same time the formation of the great new mountain chains that have arisen since the Cretaceous period.

The discussion is taken up by thirteen geologists, including Charles Schuchert, J. Joly, and J. W. Gregory, and for the most part the writers are destructively critical, though it must be remarked that the criticism is more in relation to details than general principles. The physical state of matter some 30 to 100 kilometres beneath the surface has naturally to be handled in a gingerly manner, since facts are mostly lacking, and scientific speculation is all that can be attempted.

Finally, van der Gracht sums up in a brief conclusion in which he leans decidedly towards the probability of great continental drifts, while making clear that we are only at the beginning of this study, and that it will require a generation of research and correlation of facts to enable the scientist to arrive at anything like an accurate conception of the forces that have acted and reacted in the crustal zones of the earth to bring about the present configuration of land and sea.

To review such a book which is itself a highly condensed review of a very elaborate and intricate subject, is well-nigh impossible, but some comments and suggestions may be made. It was largely the inadequacy of the cooling and contraction theory to account for mountain building that led to the idea of continental drift, and the theory has been built up gradually from the work of many writers, who since the time of Elie de Beaumont have speculated about the forms and positions of continental masses. The contraction theory could not account for regions of tension which are conclusively proved by rift-valleys, caldron subsidences, and perhaps even by salt domes. Inter- and intra-continental drift will explain such phenomena, but still leaves some puzzles with regard to mountain building, which seems to take place in what were geosynclines, where large thicknesses of sial have been accumulated and have naturally sunk deep into the sima. A drift outwards from such rooted masses of sial seems more natural than the inward lateral drive which forms mountain chains. Tidal and rotational forces seem to be very small in proportion to the vast effects attributed to them in shifting continents for thousands of miles. Joly's theory of periodical melts by the accumulated heat from radio-active forces is most attractive, and would help to explain and facilitate drifting; but it is still only a theory.

Possibly there may be other forces, at present unknown or only dimly guessed at, which may ultimately be recognised and may explain many of our difficulties. Incidentally it may seem somewhat rash to insist too much upon the permanence of both continents and ocean basins, as is the modern fashion.

However, the fact remains that built up from the work of Elie de Beaumont, Suess, Lapworth and many others the great conception of continental drift has come to stay, and a fairly strong case can be made out for it, not in all details, but on general principles.

This book is strong drink for the young or even for the experienced geologist; it may have intoxicating effects; but at least it deserves very careful reading and study. It should stimulate the reader to theorise, to collect and correlate facts, to make however small a contribution to the unravelling of these vast problems of geology.

The words of van der Gracht in his conclusion deserve reproduction here. "The entire symposium stands as token of the insufficiency of what we have been teaching in the past to explain the facts, and, also, of our inability to make our new attempts at an explanation fit in with everything which we now believe to be a fact, either in geophysics, geology or biology. J. Arthur Thompson quotes Professor Bateson's statement that our past confidence was founded chiefly on ignorance. Later generations will probably feel the same about our present beliefs. This, however, should not discourage us from always striving for the truth. If we honestly strive, we will always get a little nearer. That is all we can hope for in the realm of science in any case. The more deeply we think and search, the more problems multiply, the more our eager minds are spurred on to further activity. Is not this the essential appeal of it all, and vastly to be preferred to the attitude of the latter half of the last century, when so many thought to have solved it all?"

E. H. Cunningham Craig.

BOOK RECEIVED.

The Thomas Recording Gas Calorimeter. Fuel Research Board Technical Paper. No. 20. 1928. H.M. Stationery Office, London. 9*d*. net.

The first instrument tested was made by the Cutler Hammer Co., of New York, the investigation being carried out at the request of the Cambridge

Instrument Co. Certain defects were noted and parts of the instrument were re-designed by the latter firm. After further modification, successful results were obtained.

If properly installed and adjusted the instrument gives a reading, when working in a gas of steady calorific value, correct to ± 1 B.Th.U. When rapid fluctuations occur their full extent is not indicated, but the mean value is correct.

ERRATA.

Jnl. No. 67 (April, 1928).

Page 156, line 34. For "bulleting" read "Bulletin."

Page 158, line 7. For "experiences" read "experienced."

Page 163, line 24. For "CO2" read "CO_2."

Page 177, lines 5–10. By an omission the diagram of the window has not been shown on the first photograph. The obscuring of the window by the strengthening bands is shown by the two white lines on each flame photograph.

Page 178, line 30. For "Fig. 6" read "Fig. 2."

Page 180, line 3. For "Fig. 18" read "Fig. 15."